

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

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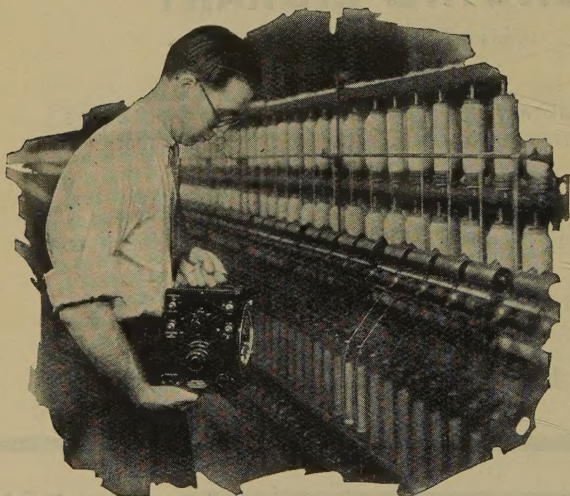
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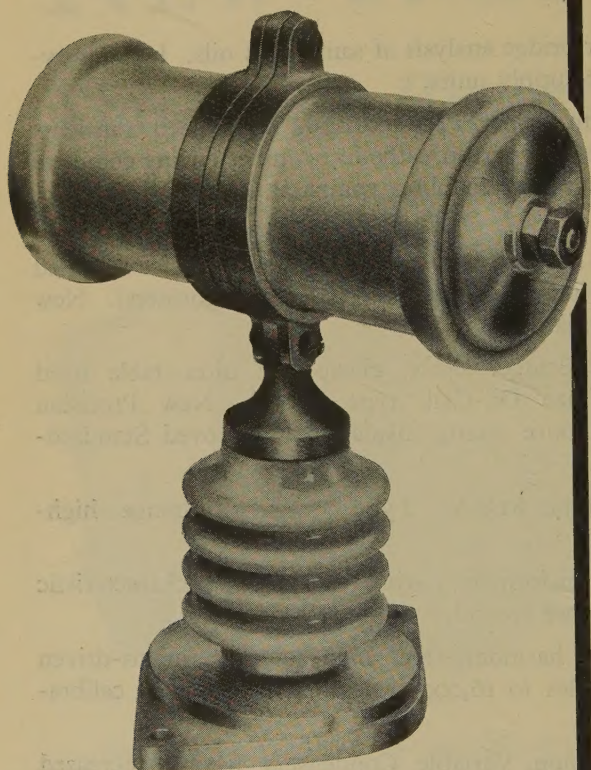
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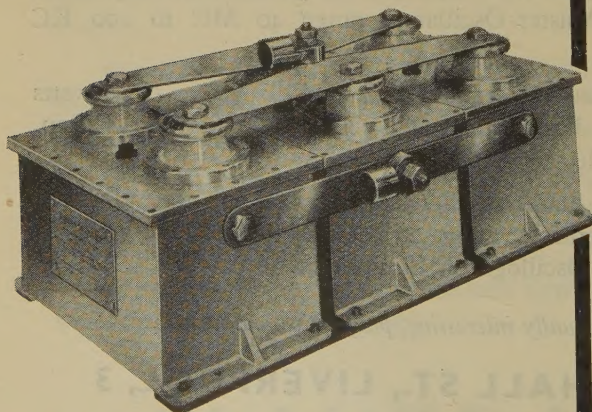
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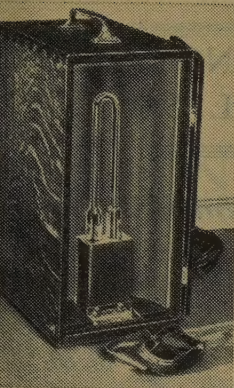
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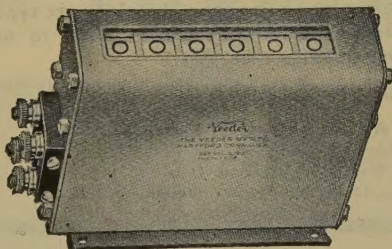
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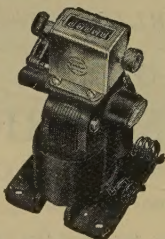
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THE PROCEEDINGS OF THE PHYSICAL SOCIETY

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WOOD-WATER RELATIONSHIPS: (I) MOLECULAR SORPTION AND CAPILLARY RETENTION OF WATER BY SITKA SPRUCE WOOD

BY W. W. BARKAS, M.Sc., Forest Products Research
Laboratory, Princes Risborough, Aylesbury, Bucks.

Received June 3, 1935. Read October 4, 1935

ABSTRACT. An attempt is made to distinguish experimentally between the amount w_a of water held by molecular sorption, and that, w_c , held by capillary retention on finely ground flour of Sitka spruce wood. The method used consists in flooding the evacuated flour with an evacuated aqueous solution of sucrose and measuring the change in concentration of the solution with an interferometer. Since capillary retention requires for its manifestation free liquid surfaces in the interstices of the wood, it is claimed that, when the vacuum method here described is used, only true molecular sorption will cause a change in concentration of the solution. Since there are indications that a certain small amount of sucrose also is adsorbed by the wood, it is impossible to arrive at the exact value of w_a , but a minimum possible value $w_{a(\min.)}$ is given which varies with the vapour pressure of the solution used, and amounts, on extrapolation to infinite dilution, to some 23 per cent of the dry weight of the wood. The difference between the total sorption W measured on the vapour-pressure isothermal and the values of $w_{a(\min.)}$ here found is taken to represent the maximum possible value for w_c .

The question of the sorption of sucrose is discussed, and the suggestion is made that the moisture-content hysteresis in w_a is smaller than that in W ; thus a greater proportion of water is held by capillary forces on desorption than on adsorption.

§ 1. INTRODUCTION

THE lowering of the vapour pressure of water held in wood can, in common with the same phenomenon in other gels, be accounted for either on the capillary theory, which holds that a low vapour pressure is due to the purely physical effect of the presence of curved menisci of the condensed phase in the small interstices of the solid phase, or alternatively on the assumption that molecular binding forces exist between the liquid molecules and those of the solid. The literature in support of each of these theories, or modifications of them, is vast, but the whole subject has been very fully discussed in McBain's *The Sorption of Gases and Vapours by Solids* (1932).

The present paper, which forms part of the work comprised in Project 8 of this Laboratory, is concerned with an attempt which was made to distinguish experimentally between these two theories as applied to the sorption of water by wood.

Previous works on wood-water relationships bearing on the question of sorption are not numerous. Pidgeon and Maass⁽¹⁾, Lavine and Gauger⁽²⁾ and Seborg and Stamm⁽³⁾ have measured the vapour-pressure isothermals of various woods in the form of small pieces or of fine flour and found the curves to be identical in shape, though not in numerical values, with those for cotton⁽⁴⁾ and similar materials. Stamm and Loughborough⁽⁵⁾ have made use of these curves in studying the thermodynamics of the swelling of wood. The work of Pidgeon and Maass has a direct bearing on the present discussion, since the authors conclude that molecular sorption accounts only for the low vapour-pressure values up to a moisture-content of about 2 per cent, before the hysteresis appears, and that the sorption in the hysteresis region is entirely capillary. They calculate from the Thomson equation⁽⁶⁾ that the radius of the menisci at the lower end of this range is 4.5×10^{-8} cm. and that "near the saturation point" it is 3.8×10^{-6} cm.* Lavine and Gauger account for the differences between the vapour-pressure isothermals of various substances entirely in terms of the distribution of capillary magnitudes, while Stamm and Loughborough take the point of inflection on the isothermal as the approximate transition point between the two forms of sorption and say: "This relative vapour pressure gives a capillary radius... that is only 2.3 times the molecular diameter. This is very near the limiting distance expected for primary molecular attraction and should represent the limiting size of capillary in which capillary condensation can take place." Now it is evident that since the lower value calculated by Pidgeon and Maass is only twice the diameter of the hydrogen molecule and only half the narrow axis of the cellulose molecule⁽⁷⁾, it is impossible to construct either a circular cavity of these dimensions surrounded by such large units, or a hemispherical water-surface inside it. The same difficulty applies almost equally to the calculation of Stamm and Loughborough. Since the derivation of the Thomson formula assumes a spherical meniscus, we must, for this reason alone, dismiss the quantitative validity of the calculation. This does not, however, rule out the capillary theory as a qualitative explanation of sorption at the higher vapour pressures because, though we may reasonably expect both the density and the surface tension of the water to be modified by its close association with the capillary wall⁽⁸⁾, it is none the less true that a concave meniscus of any shape will result in a lowered vapour pressure, though its shape may be too complicated for mathematical computation. Another point in favour of the capillary theory is, as has been pointed out by Zsigmondy⁽⁹⁾, that it very neatly explains the hysteresis between wetting and drying as being due to the fact that the delayed wetting of the capillary wall in the adsorption cycle results in a flattened meniscus and a higher vapour pressure. The true Thomson effect is observed only on desorption when the capillary walls are wet and the menisci hemispherical.

The argument leading up to the method used here to differentiate between moisture held by capillary forces and that held by molecular sorption is as follows. The capillary theory requires, for the manifestation of lowered vapour pressure, the

* Since at complete saturation these radii must be infinite, the authors presumably refer to the highest values of the vapour pressure which they actually measured.

presence of free water-surfaces, or more strictly air-water or vapour-water interfaces, in the interstices of the material, while the molecular theories will admit of a bond between the water and the wood even if no such interface exists—that is to say even when the wood is completely immersed in water. Hence any method which can demonstrate sorption when the wood is completely impregnated, without the possibility of free water-surfaces occurring, will be measuring molecular sorption and will ignore capillary retention. Since the total sorption at any vapour pressure is given by the vapour-pressure isothermal, any difference between this total and that proved to be molecular sorption may reasonably be put down to capillary forces. It should be noted that this method of distinction is purely experimental and does not require any assumption as to the nature of the molecular sorption nor the quantitative validity of the Thomson formula.

In the method adopted, samples of wood flour, ground sufficiently fine to ensure the cell structure being broken down, were evacuated till the dry weight was constant. This dry flour was then saturated in a vacuum with an aqueous sucrose solution of known concentration, which had also been evacuated as completely as possible. When the flour was completely immersed, the apparatus was opened to the air so that a pressure of 1 atmosphere forced the solution into the interstices of the wood wall. If molecular sorption occurred, water would be abstracted from the solution and held by the wood, thus leaving the solution at a slightly higher sugar-concentration than before. Capillary retention, on the other hand, would not be measured because no free menisci would be available for its manifestation. Thus if W is the total weight of water held by 1 g. of the wood as determined from the vapour-pressure isothermal, and w_a is the weight of water held by molecular sorption per gram of wood, then the difference is the weight w_c held by capillary forces, thus

$$W - w_a = w_c \quad \dots\dots(1).$$

W
 w_a
 w_c

The present research, which was begun in 1931, was inspired by the work of Newton and Gortner⁽¹⁰⁾ on the bound water in vegetable tissues. Their method showed the value of sucrose as an indicator of sorption, but they did not adopt a vacuum technique. This meant that the penetration of the material by the solution might be incomplete, free liquid surfaces might occur, and capillary retention might result by vapour diffusion from the solution across the air spaces. Their method was to measure the lowering of freezing-point of the solution and from it to calculate the amount of water abstracted, but this meant working at temperatures lower than those usually met with in practice, and with such quantities as would ensure a large change in concentration of the solution. Interferometer measurement of concentration-changes was therefore adopted, as it was suitable to any temperature, and concentration-changes as low as 0.01 per cent of sugar could be measured with reasonable accuracy. A report on the preliminary results of this work appeared in 1932⁽¹¹⁾, and the use both of sugar solution as an indicator and of the refractometer for measuring changes in concentration has been extended by others^(12, 13, 14); but so far as the author is aware no attempt has been made on the present lines to differentiate between molecular sorption and capillary retention.

§ 2. THEORY

Let X be the dry weight of flour, M the weight of solution added, C_1 the initial concentration of sucrose solution in grams of sucrose per gram of solution, C_2 the concentration of the solution after sorption, ΔC the change ($C_2 - C_1$) in concentration, and s the weight of sugar held by molecular sorption per gram of wood.

Initially we have $C_1 M$ g. of sugar and $(1 - C_1) M$ g. of water in the solution. After adsorption there are $(C_1 M - Xs)$ g. of sugar and $(1 - C_1)(M - Xw_a)$ g. of water in the solution.

Therefore
$$C_2 = \frac{C_1 - Xs}{(1 - C_1)M - Xw_a + C_1 M - Xs},$$

so that
$$w_a = \frac{M\Delta C + Xs(1 - C_2)}{C_2 X} \quad \dots\dots(2).$$

When the wood and sugar solution reach equilibrium, the aggregate (wood + sorbed water + sorbed sugar) must be in thermodynamic equilibrium with the remaining solution at its final concentration C_2 ; that is to say they must exert the same vapour pressure. Hence if s were known for different values of C_2 , a vapour-pressure isothermal for w_a could be built up by using solutions of different concentrations whose vapour pressures may be obtained from tables. Now s is in fact unknown, but if it is assumed to be zero, equation (2) above shows w_a will then have its minimum value which we may call $w_{a(\min.)}$. Thus equation (2) may be written

$$w_a = w_{a(\min.)} + s(1 - C_2)/C_2 \quad \dots\dots(3),$$

where $w_{a(\min.)} = M\Delta C/C_2 X$ and is the smallest possible value of w_a . The second term represents the amount to be added to $w_{a(\min.)}$ to give the true molecular sorption if s were known. Thus w_c cannot be greater than $W - w_{a(\min.)}$, and could be zero.

§ 3. MATERIALS

Blocks of Sitka spruce (*Picea Sitchensis* Carr.) were cross-cut and sifted to produce a fine sawdust whose mesh-size lay between 60 and 100. This was extracted for 48 hours at 20° C. distilled water with constant stirring, when on further shaking with distilled water the liquid showed no change in refractive index to the fifth place of decimals. The extractives removed in this way amounted to 0.75 per cent of the dry weight of the wood. After extraction the flour was air-dried without heat and stored in air-tight bottles. This method ensured a supply of material of great uniformity and was used for the whole of these experiments.

Pure analytical-reagent sucrose crystals, $C_{12}H_{22}O_{11}$, were used for the solutions, which were made up fresh to approximate strength as required. As soon as they had been prepared the solutions were put into the sorption apparatus K , figure 1, and evacuated till the residual air pressure, measured on a McLeod gauge, was less than 0.005 mm. of mercury. As freezing methods were not available, this evacuation was effected by evacuating a large vessel L , some 100 times the volume of the vessel containing the solution, and then putting L and K into communication.

In this way the pressure was reduced at each operation to about one hundredth of the difference between the pressures in the two vessels, whereas the loss of water was only the weight of vapour required to saturate the larger volume. Since the concentration of the solution was measured on a sample taken later in the experiment, this loss does not affect the results.

§ 4. APPARATUS

A sample of wood flour weighing about 1 g. was contained in each of the three bottles *A*, figure 1. These bottles, which had a capacity of about 25 cm³, could be closed by the tap *B* and removed, while evacuated, at the ground-glass joint *C*, of which the inner half was connected to the bottle to facilitate the removal of the tap grease before weighing. The outer halves of the joints *C* were joined by *D* to the two-way tap *E*, one side of which led past a mercury manometer to the drying-tube *F*, which contained P₂O₅, and thence to the McLeod gauge and the Hyvac rotary pump. The other side of *E* (not shown) served to admit air when the bottles

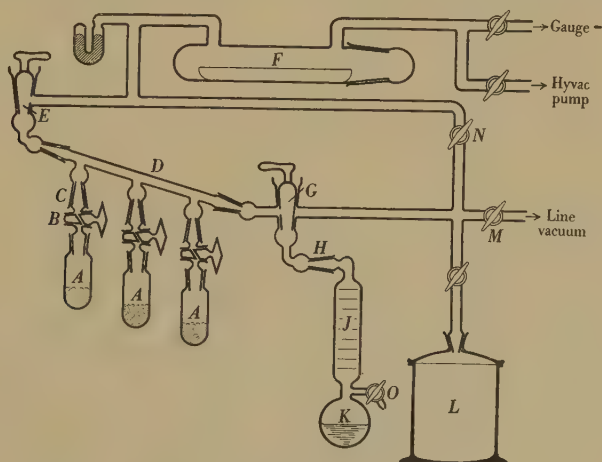


Figure 1. Diagram of apparatus.

had to be weighed. The other two-way tap *G* led down to a horizontal ground-glass joint *H* which held a graduated tube *J*, about 20 cm. long, on the end of which was a bulb *K* containing about 100 cm³ of solution. The other branch of *G* led through the large vessel *L* to the tap *M*, and thence to drying tubes (not shown) and a service vacuum.

With *J* and *K* hanging down in the position shown, the solution could be evacuated first through *M* and later through *N* and *F* to the high vacuum in the manner described above, but when *J* was turned about the joint *H* through 180°, the solution ran down into *J*. With *E* and *B* closed, the tap *G* was opened to *D* which was thus completely filled with solution. By noting the level of the solution in *J*, any required volume could be admitted to the bottles *A*, the exact amount being determined by subsequent weighing.

The tube *D* was slightly inclined so that any minute bubbles would rise to the tap *E* and would not enter the bottles. These bubbles are at the pressure of the evacuated system, and do not represent poor evacuation of the apparatus. The small side-tube and tap at *O*, between *J* and *K*, served to admit air after the experiment.

A few points with regard to the bottles *A* require special notice. The bore of the holes in the taps was slightly enlarged at the ends so as to give a small space in which surplus tap grease could collect and not be drawn into the bottle by the rush of liquid on opening. The ground stoppers of the bottles had grooves round the lower ends of the ground surfaces and the grease was spread only above these grooves. In this way the surplus grease was enabled to squeeze into the grooves and could not mix with the solution in the bottles. The diameter of the bottles was such that when the stopper was replaced by a rubber cap the bottles themselves could be used as centrifuge tubes for separating out the flour from the solution.

It may be of interest to note that an accurate Rayleigh interference refractometer was constructed by using the tilt movement of a theodolite for mounting the compensating glasses. These, if 1 mm. thick, give a fringe movement of about $\frac{1}{10}$ of a fringe to 1 min. of arc of tilt of the compensator. The only parts which were specially bought for the instrument used here were the optically worked compensating-glasses and the special one-piece double-compartment cell for the liquids. The range covered was ± 0.0017 in the value of μ .

§ 5. PROCEDURE

The vacuum bottles together with the grease on the tap and the neck were evacuated and weighed. After about 1 g. of wood flour had been introduced into each bottle, the bottles were evacuated over the phosphorus pentoxide in *F* and weighed daily until a loss of water smaller than the experimental error, 0.2 mg., was registered. This gave *X*, the dry weight of the flour, equation (2). After prolonged evacuation to a pressure less than 0.005 mm. of mercury, the bottles were filled with solution and, as soon as the first one was detached, a sample of the solution was poured direct from the joint *C* into one of the two cells of the Rayleigh interference refractometer and a few drops were taken for the determination of the refractive index on the Abbé refractometer, which after temperature corrections gave the value of C_1 to 0.1 per cent from tables⁽¹⁵⁾. The necks of the bottles were flushed out and dried and the bottles were weighed to obtain *M*, the weight of solution. The small amount of solution held in the bore of the tap was negligible. The taps *B* were now opened so as to allow the atmospheric pressure to force the solution into the wood. In most of the experiments the bottles were completely filled with solution, so that if they were slowly rotated the flour and solution could be mixed without the introduction of air into the mixture. Experiment showed that the measured sorption was completed in less time than was necessary for manipulation (about 20 min.), and that the opening of the bottles to the atmosphere as described above did not affect the results, so that actually the atmospheric pressure is not

necessary for complete impregnation. Thus smaller quantities of solution could be used and the bottle could be shaken before being opened. With the more dilute solutions, the wood flour settled out in about half an hour and a sample of the supernatant liquid was then taken direct from the bottle to the other cell of the Rayleigh interferometer. With stronger solutions the sediment was centrifuged out, the bottle itself serving as centrifuge tube; thus errors due to evaporation were removed. The following tests were made to discover errors arising in the course of manipulation. (i) The use of empty bottles and distilled water showed that no detectable change in refractive index occurred as a result of solubility of the tap grease. (ii) The use of empty bottles and sugar solution also showed no detectable change in refractive index; this proved that evaporation losses, or sorption on the glass and the tap grease, were negligible. (iii) The use of wood flour and water showed that the extractives had been removed sufficiently well for the refractive-index change to be less than 0.00001.

The temperature of the apparatus was not regulated, but the solutions were shaken and centrifuged on the concrete floor of the laboratory, the temperature being usually between 19° and 20° C. and the maximum variations from 17.5° to 21° C.

§ 6. MEASUREMENT OF ΔC

After the two samples had stood in the interferometer for 2 hours, the difference $\Delta\mu$ between their refractive indices was measured to 0.00001 by taking the mean of the two values of $\Delta\mu$ given with the cells in the direct and reversed positions, the necessity for an exact determination of the zero of the instrument being thus removed. It was found that when the cells were left standing there was a tendency for concentration-gradients to be set up in them owing to moisture evaporating and condensing at the tops of the cells. Before a reading was taken, therefore, the cells were shaken to remix the solutions in each compartment. The correction in $\Delta\mu$ for the thickness of the walls of the empty cells amounted to 0.00012 and was applied to all readings. There was found to be no detectable error due to difference between the thicknesses of the cells themselves.

The conversion of $\Delta\mu$ to ΔC could not be carried out directly since tables only give μ to 0.0001 and C in steps of 0.1 per cent, so differences of μ for 1-per-cent changes in concentration were taken and $\Delta C/\Delta\mu$ was plotted against the concentration at the centre of the range. In this way a large-scale graph of $dC/d\mu$ was obtained with very definite values from $C=80$ per cent (in grams of sugar per gram of solution) to $C=10$ per cent, while a less definite line could be traced to $C=5$ per cent. It was found that Schönrock's tables⁽¹⁶⁾ gave a much smoother curve than Main's tables⁽¹⁵⁾, owing to slight differences in the fourth place of decimals, and they were, therefore, used for this purpose.

From this curve we have $(dC/d\mu) \Delta\mu = \Delta C$ while $C_1 + \Delta C$ gives C_2 . The data necessary for the calculation of the $w_{a(\text{min.})}$ of equation (3) are thus completed.

 $\Delta\mu$

§ 7. RESULTS

Since each concentration of sugar gives a different vapour pressure with which the wood + water + sugar aggregate must be in equilibrium, we may expect different values of $w_{a(\text{min.})}$ to be obtained for different concentrations, and this has proved to be the case.

Table 1

Reference	M/X	C_2	ΔC	$w_{a(\text{min.})}$	Relative vapour pressure of solution C_2	W at same relative vapour pressure
86/1	26.31	0.3533	+0.00233	0.175	0.9685	0.279
86/2	27.48		+0.00236	0.183		
88/14	28.58		+0.00186	0.186		
88/16	29.03		+0.00182	0.186		
88/15	27.56	0.1888	+0.00187	0.180	0.9775	0.296
98/13	54.55		+0.00065	0.189		
98/11	51.9		+0.00071	0.195		
98/12	56.8		+0.00065	0.196		
82/13	25.22	0.1783	+0.00141	0.202	0.9872	0.325
82/11	25.21		+0.00141	0.200		
82/12	27.15		+0.00135	0.206		
100/4A	25.11		+0.00086	0.215		
100/7	22.31	0.1029	+0.00096	0.208	0.9882	0.339
100/9	24.52		+0.00086	0.210		
9/13	25.28		+0.00079	0.2025		
9/12	26.02		+0.00077	0.2035		
92/4A	24.32	0.0554	+0.00049	0.214	0.9943	0.356
92/7	24.26		+0.00049	0.2135		
92/9	23.79		+0.00049	0.2100		
		0.0988	+0.00079	0.2025	0.9945	0.357
			+0.00077	0.2035		
		0.0554	+0.00049	0.214	0.997	0.370
			+0.00049	0.2135		
			+0.00049	0.2100		

In table 1 are given the results for each separate determination, grouped in sets representing separate runs of (usually) three bottles. The values of C_2 and ΔC are given as grams of sugar per gram of solution, while M/X is the weight-ratio of solution to wood flour. The last column gives the value of the equilibrium moisture-content for the same wood flour at the relative vapour pressure of the solution used, these values being taken from measurements of the vapour-pressure isothermal of Sitka spruce flour at 20° C., figure 4. A detailed description of the measurement of the isothermal will be given elsewhere, in a paper more concerned with its exact determinations⁽¹⁷⁾, when the most reliable results are obtainable. It is sufficient to say here that the present figures for the moisture-content are unlikely to be in error by more than 2 per cent. The measurements were made on wood flour which had, as here, been previously evacuated to dryness.

§ 8. THE EFFECT OF THE INITIAL MOISTURE-CONTENT OF THE WOOD FLOUR

If the wood flour initially has a moisture-content m grams of water per gram of dry flour, equation (2) becomes

$$w_a' = \frac{M\Delta C + Xs'(1 - C_2)}{C_2X} + \frac{m}{X},$$

$$= w_{a'(\min.)} + \frac{s'(1 - C_2)}{C_2} \quad \dots\dots(4),$$

where the dashes refer to the desorption process. Provided that the value of m is sufficiently high for the sign of ΔC to be reversed when the solution is mixed with the flour, desorption results and the solution becomes less concentrated.

A few experiments were made with flour having a known initial moisture-content above the minimum saturation value. After the dry weight of the flour had been obtained as before, the bulb K , figure 1, was filled with evacuated water. K was warmed and the bottles A were cooled, free distillation on to the flour being thus brought about. After m had been determined by weighing, the water was replaced by sucrose solution and the experiment proceeded as before.

Table 2 shows the values of $w_{a'(\min.)}$ so obtained.

Table 2

Reference	M/X	m	C_2	ΔC	Relative vapour pressure of C_2	$w_{a'(\min.)}$
102/1	49.9	0.717	0.3019	-0.00311	0.9735	0.203
102/2A	28.1	0.577	0.3011	-0.00385	0.9745	0.219
102/3	25.2	0.671	0.2993	-0.00566	0.9762	0.194
					Mean	0.205
104/4A	24.6	0.542	0.1615	-0.00209	0.990	0.223
104/7	24.4	0.516	0.1616	-0.00196	0.990	0.220
104/8	24.7	0.490	0.1617	-0.00189	0.990	0.202
					Mean	0.215

The mean values of $w_{a'(\min.)}$ are higher than the corresponding values of $w_{a(\min.)}$ for the dry flour, and this shows that a hysteresis in $w_{a(\min.)}$ occurs similar to that found in the isothermal itself, but owing to experimental difficulties there is considerably more scatter between the individual readings, which makes the true determination of $w_{a'(\min.)}$ less precise.

§ 9. DISCUSSION OF RESULTS

By extrapolating the values of $w_{a(\min.)}$ or $w_{a'(\min.)}$ to 100 per cent relative vapour pressure, it may be taken that the limiting value of either of these quantities is about 23 per cent of the dry weight of the wood, or rather more than half of the total sorption W in a saturated atmosphere. It is thus evident that the minimum

amount of water held in the wood by molecular sorption and not by capillary forces forms a larger proportion of the total sorption than that deduced by the authors previously mentioned^(1, 2, 3); and it must always be remembered that the actual proportion may be larger still if sugar sorption is present.

There is, however, a possible objection to the method used which may be raised, and it will be well to consider it here before dealing with the question of the sorption of sugar. It may be argued that the fine capillaries of the wood substance act as a filter to the solution, allowing the small water molecules to enter but being too fine to admit the larger sugar molecules. If this is so, then it is true that ΔC will be effected in the way and in the degree observed in these experiments. If, however, the effective radius of the sugar molecule in solution were known and were taken as the diameter of the smallest capillary which would admit sugar, it would be possible from the Thomson equation and the vapour-pressure isothermal to determine the moisture-content below which this filter action would operate. On the capillary theory, therefore, this moisture-content should correspond to the values of the so-called molecular sorption measured in these experiments. There is no precise information as to the dimension in question, but from the X-ray measurements of the crystallographic axes of sucrose we obtain a figure which will be larger than the sucrose molecule itself and which will therefore give too high a value for the moisture-content at which filter action could occur. Taking the largest axis of the sucrose molecule as 10.6×10^{-8} cm.⁽¹⁸⁾, we obtain from the Thomson equation a vapour pressure corresponding to a moisture-content of only about 7 per cent. These experiments, on the other hand, show sorptions up to a moisture-content of 21 per cent with solutions of 97 per cent relative vapour pressure corresponding to a capillary radius of 360×10^{-8} cm. Thus the argument is untenable unless the molecular aggregation of sucrose in solution is more than 68 crystal units in diameter or about 165,000 in spherical volume. The number of molecules in the aggregate would have to be still greater in view of their smaller size.

A second possible argument is that the cellulose molecule in wood is generally considered to be of a long polar form grouped into bundles or micellae, and that water is attached to the side chains of these molecules. It may, therefore, be argued that the water is held not in cylindrical holes but in parallel-walled slits between one layer of molecules and the next, making the meniscus not spherical but cylindrical. Assuming the validity of the Thomson equation, and following the derivation of the formula given by v. Helmholtz⁽¹⁹⁾, we can show that to exert a given vapour pressure the radius of such a cylindrical meniscus must be one half that of a spherical meniscus. This will still mean, however, that about 20,000 crystal units of sugar must be grouped if they are not to enter a pore giving a relative humidity of 97 per cent. This assumption of a cylindrical meniscus in a parallel-walled slit has the counterbalancing disadvantage that, at low vapour pressures, the calculated sizes are even smaller in relation to molecular dimensions, so that the theory becomes even less acceptable. Thus the only ground left for assuming that the effect here measured is due to a filter action must be that even at vapour pressures approaching saturation the value of the radius given by the Thomson

uation is some thirty-five times too small, whereas it is precisely at the higher pour pressures that this equation becomes quantitatively acceptable.

§ 10. THE SORPTION OF SUGAR

If the true molecular sorption w_a of the water were known, the sorption s of gar could be obtained by writing equation (3) thus

$$s = \frac{C_2 (w_a - w_{a(\text{min.})})}{1 - C_2} \quad \dots\dots(5).$$

As was pointed out above, w_a is not known but must lie between the value $w_{a(\text{min.})}$, which it has when s is zero, and W , the value found from the vapour-pressure thermal. $w_a = W$ corresponds to the maximum value of s which we may call $s_{\text{max.}}$. In table 3 the results shown in table 1 are again used to calculate the maximum

$s_{\text{max.}}$

Table 3

Reference	C_2	$w_{a(\text{min.})}$	W	$s_{\text{max.}}$	Mean value of $s_{\text{max.}}$
86/1	0.3533	0.175	0.279	0.0568	0.0547
86/2		0.183		0.0525	
88/14		0.186		0.0440	
88/16	0.2859	0.186	0.296	0.0440	0.0448
88/15		0.180		0.0465	
98/13		0.189		0.0319	
98/11	0.1888	0.195	0.325	0.0303	0.0310
98/12		0.196		0.0308	
82/13		0.202		0.0297	
82/11	0.1783	0.200	0.339	0.0302	0.0299
82/12		0.206		0.0298	
100/4A		0.215		0.0162	
100/7	0.1029	0.208	0.356	0.0170	0.0166
100/9		0.210		0.0168	
90/13		0.2025		0.0169	
90/12	0.0988	0.2035	0.357	0.0168	0.0168
92/4A		0.214		0.00913	
92/7		0.2135		0.00913	
92/9	0.0554	0.2100	0.370	0.00938	0.0093

sorption of sugar, by assuming that $w_a = W$. Figure 2 gives graphically the relation $s_{\text{max.}}$ to the concentration of the solution, showing that the mean values lie on almost straight line which passes through the origin, as we should expect. This simple relation between $s_{\text{max.}}$ and C affords, however, no evidence that w_a is in fact equal to W , because a similar relationship would also hold if w_a were, at each vapour pressure, any simple fraction of W . The values of s would then be reduced in the same ratio.

Hitherto it has been tacitly assumed that the water and the sugar are sorbed independently, so that the water in the wood+water+sugar aggregate exerts a vapour pressure equal to that exerted by the same quantity of water in the simple case where only wood and water are present. To test the validity of this assumption

a sample of wood flour was flooded with distilled water in which sugar weighing 4 per cent of the dry weight of the flour had been dissolved. This was evaporated to dryness *in vacuo* without heat to give an intimate mixture of wood and sugar in

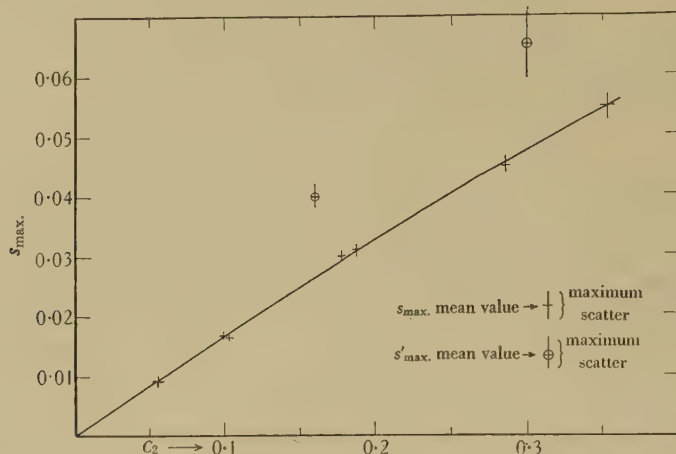


Figure 2. Curve relating s_{\max} with C_2 .

the above proportions. The isothermal of this mixture was determined simultaneously with that of a control sample of flour treated with distilled water only, so that differences between the moisture-contents of the two samples at the same

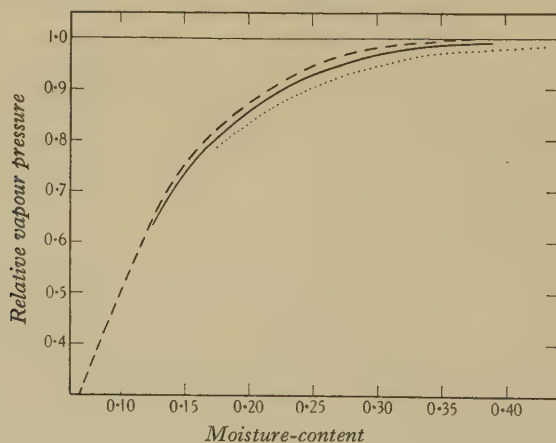


Figure 3. Adsorption isothermal of wood flour + 4 per cent of sucrose at 20° C. Wood flour only -----; Wood + 4 per cent of sugar, experimental ———; Wood + 4 per cent of sugar, calculated

vapour pressures might be accurately determined. In figure 3 the isothermal of the wood alone is shown as a broken line, based upon table 2, and that of wood + 4 per cent of sugar is shown as a full line. The dotted line shows the curve which would have been obtained had the wood and sugar each held its full complement of water independently. It is thus evident that the action of the sugar is not independent of that of the wood, and we may therefore conclude that (i) sugar is

erbed by the wood, (ii) $w_a > w_{a(\min.)}$, and (iii) the values of s shown in figure 2 are too large.

The isothermal of the ternary mixture shown in figure 3, while demonstrating the sorption of sugar, does not help in fixing the exact value of w_a because, as in the case where wood and water only are concerned, it is the total sorption by the wood and sugar that is measured, and no indication is given as to the proportion of this that is due to either the wood or the sugar separately.

When we make the attempt to get beyond the present position of knowing a minimum value for w_a and a maximum value for s the argument becomes much more speculative, but with this proviso a little more information may be gained from further study of the values of $w_a'(\min.)$ found for desorption. Figure 4 shows the

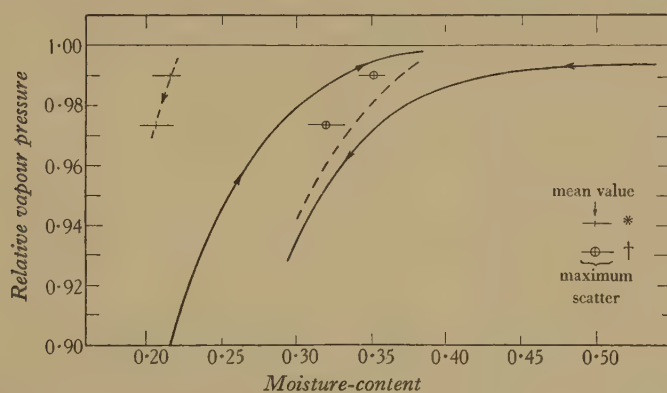


Figure 4. Adsorption and desorption isothermals of Sitka spruce flour at 20° C.

* $w_a'(\min.)$; † $w_a'(\max.)$.

upper values of the isothermal both for adsorption and desorption. The latter values were measured on the same sample as the former, but the moisture-content was raised above the minimum saturation value by free distillation of water on to the flour till it exceeded 90 per cent. On drying by small steps a measurable drop in the vapour pressure occurred at moisture-contents much in excess of the sorption-saturation value, showing that the hysteresis persists even at the saturation vapour pressure. The dotted line shows the commonly accepted shape of the hysteresis loop, which is usually obtained by extrapolation from lower desorption values and would probably be found on desorption from the fibre-saturation moisture-content of about 40 per cent.* This effect of hysteresis at saturation will be dealt with in a later publication⁽¹⁴⁾, but it is important for the present discussion that the calculation of s' is to be attempted for the water-desorption cycle, since we are now starting from high moisture-contents. Table 2 showed that a hysteresis exists

* The term *fibre-saturation point* is defined to mean the moisture-content of wood when the cell wall is saturated but the cell spaces are empty. The point must correspond to the minimum moisture-content in equilibrium with a saturated atmosphere. Other work at this Laboratory⁽¹⁷⁾ indicates that this equilibrium moisture-content is not a simply defined point and that further research is required. The fibre-saturation point is here taken provisionally as the moisture-content reached at 95 per cent relative vapour pressure in the adsorption process, which for Sitka spruce flour is about 40 per cent at 20° C.

between $w_{a(\min.)}$ and $w_{a'(\min.)}$, the wetting and drying values of the minimum molecular sorption. This hysteresis is not, however, necessarily due to differences in the sorption of water, since the measured values of $w_{a(\min.)}$ and $w_{a'(\min.)}$ are affected by the sorption of sugar. Further, it is to be remembered that in the case of s_{\max} the water and sugar are adsorbed simultaneously, whereas in that of s'_{\max} the adsorption of sugar is coincident with the desorption of water because the wood had initially an artificially high moisture-content. This poisoning⁽²⁰⁾ of the surface by the previous sorption of water would lead one to expect that s'_{\max} would be smaller, rather than greater, than s_{\max} for a given final concentration C_2 . If, however, we calculate s'_{\max} from the values of W' shown in the desorption curve in figure 4, we obtain the values given in table 4, column 6, which are found to be greater than the corresponding values of s_{\max} , column 7, taken from figure 4. This is sufficiently improbable to suggest that whatever the ratio w_a/W , the corresponding ratio $w_{a'}/W'$ is smaller; which means that the hysteresis loop for molecular sorption is narrower than that for total sorption.

Table 4

1 Reference	2 m	3 Relative vapour pressure of C_2	4 $w_{a'(\min.)}$	5 W'	6 s'_{\max}	7 s_{\max}	8 $w_{a'(\max.)}$ derived from s_{\max}
102/1	0.717	0.973	0.203	0.353	0.0648	0.0480	0.319
102/2 A	0.577	0.974	0.219	0.356	0.0590	0.0477	0.332
102/3	0.671	0.976	0.194	0.361	0.0714	0.0475	0.305
	Means	0.974	—	—	0.0651	0.0477	0.319
104/4 A	0.542	0.990	0.223	0.420	0.0380	0.0265	0.359
104/7	0.516	0.990	0.220	0.420	0.0393	0.0265	0.355
104/8	0.490	0.990	0.202	0.420	0.0421	0.0265	0.338
	Means	0.990	—	—	0.0398	0.0265	0.351

The shape of the desorption curve in figure 4 supports the view that, at artificially high moisture-contents, a large proportion of the water is held by capillary forces. To simplify the argument which follows we shall assume that the pores in the wood consist of circular holes of uniform cross-section but of varying sizes. There is actually no evidence to prove that this is so, but qualitatively the effect will be the same whatever the shape of the holes. Initially the wood contains in its interstices free water which, being in equilibrium with the saturated vapour pressure, must have flat surfaces. On evaporation of a small quantity of water these surfaces will at once become concave, giving the reduced vapour pressure corresponding to the drop in vapour pressure associated with a very small loss of water. This will occur on desorption whatever the initial moisture-content between the adsorption fibre-saturation point and complete saturation of the wood. The second stage commences when the radius of curvature of the menisci equals that of the largest pores in the wood. At this point the largest pores begin to empty, and since by the Thomson equation the rate at which the vapour pressure changes with curvature of meniscus is small for large capillaries, considerable loss of water

from the largest pores will be associated with only a small further drop in vapour pressure. This accounts for the shape of the desorption isothermal down to a moisture-content of about 40 per cent.

Hence there are good grounds for assuming that, on the desorption curve, at least all the water in excess of the adsorption fibre-saturation point is held by capillary forces, from which it follows that $w_a' < W'$ and that the values of s'_{\max} in table 4, column 6, are too high. If this reasoning is sound we may now deduce an upper limit for w_a' , which we may call $w_{a'(\max.)}$, from the improbability of the sugar adsorption being greater when water is initially present than when water and sugar are adsorbed simultaneously. These values are given in table 4, column 8, and are obtained by calculating $w_{a'(\max.)}$ from equation (2), using the value of s_{\max} found from the adsorption experiments, column 7. The lower limit to w_a' remains equal to $w_{a'(\min.)}$ as given in column 4. $w_{a'(\min.)}$ and $w_{a'(\max.)}$ are plotted in figure 4.

If more experiments had been made with previously moistened wood flour over a wider range of solution-concentrations C_2 , the values of $w_{a'(\max.)}$ could have been determined more accurately, but it hardly seems worth while to do this in view of the fact that the possible limits of w_a' are in any case fairly wide and the experimental difficulties considerable. The experiments here recorded are sufficient to show that the hysteresis loop in w_a is narrower than that in W , and that therefore more water is held by capillary forces on desorption than on adsorption.

§ II. ACKNOWLEDGMENTS

In conclusion the author wishes to record his indebtedness to Prof. A. W. Porter, F.R.S., for his valuable criticisms of this work while it was in progress, to Mr W. A. Robertson, Director of the Forest Products Research Laboratory, for permission to publish the paper, and to the Chemistry Section of the Laboratory for its co-operation.

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APPENDIX ADDED OCTOBER 17, 1935

Measurements made on the unextracted flour of the same batch of Sitka spruce were not included in this paper, partly because the experimental difficulties were such as to lower one's confidence in the accuracy of the results, but chiefly because an accurate isothermal for the natural wood was not available when the paper was submitted. Since then I have found that the isothermal of natural white spruce has recently been measured by Filby and Maass, and as this curve agrees well with my less accurate measurements on natural Sitka spruce I think it may serve as a basis of calculation.

Before the calculation of w_a can be made for natural wood, a correction has to be applied for the refractive index of the cold water extractives which will dissolve in the sugar solution. This was done by first comparing with pure water the refractive index of the flour-water mixture and then making sure that the change of refractive index due to the extractives was the same in pure water as in a sugar solution. For the first test different proportions of flour and water were shaken together *in vacuo* for different times. It was thus shown that, for the range of flour-solution ratios used in the experiments to be described, the extractives were completely dissolved in about 2 hours and gave a refractive-index change equivalent to 0.00160 for 1 g. of flour per 1 g. of water. Hence the correction for any flour-water ratio could be calculated. For the second test, samples of the solution of the extractives which had been removed from the flour used in the main experiments, page 4, were mixed in equal volumetric proportions with (a) pure water, (b) 8-per-cent sugar solution, and (c) 19-per-cent sugar solution. It was found that the refractive-index change was sensibly equal in each case so that the refractive index due to the extractives was volumetrically additive to that of the sugar solution.

Table 5 gives the results in the same way as does table 2 in the main paper, page 9, with the addition of W from the isothermal and the calculated values of s_{\max} , as in table 3, page 11.

If s_{\max} is plotted against C_2 it will be found that the means of the points for s for dry flour lie almost exactly on the line shown in figure 2, except in the case of the most concentrated solution, while for the flour with a high initial moisture-content the means of s' lie at values roughly corresponding to those for s' in figure 2 but, as in the case of the extracted flour, the scatter is considerable owing to experimental difficulties. For s' also the points for the highest concentration are high compared with the values shown in figure 2, but the necessity of correcting for the refractive index of the extractives considerably increases the possibility of experimental error, so it is possible that this observation is due to pure coincidence.

In general we may conclude that for the natural wood the results are almost identical with those for extracted wood, and therefore that the proportions of water held by molecular sorption are identical. This is borne out by the fact that the isothermals are also practically identical in each case.

Table 5

Reference	M/X	m	C_2	ΔC	Relative vapour pressure of C_2	w_a (min.)	W	$s_{\max.}$
(a) Dry flour								
116/13	24.91	Zero	0.3938	0.00277	0.962	0.175	0.291	0.0754
116/11	26.41	"	0.3938	0.00281		0.189		0.0662
116/12	25.50	"	0.3937	0.00269		0.174		0.0760
70/4A	28.38	"	0.1973	0.00148	0.986	0.213	0.330	0.0288
70/7	23.53	"	0.1971	0.00171		0.204		0.0306
70/8	22.27	"	0.1971	0.00167		0.189		0.0346
76/1	23.31	"	0.1940	0.00169	0.987	0.204	0.331	0.0306
76/2A	26.32	"	0.1942	0.00148		0.201		0.0314
76/3	22.69	"	0.1940	0.00169		0.197		0.0323
56/4	11.97	"	0.1676	0.00302	0.989	0.217	0.350	0.0268
56/5	12.23	"	0.1675	0.00307		0.225		0.0252
56/9	12.32	"	0.1679	0.00272		0.202		0.0299
(b) Wet flour								
						w'_a (min.)		$s'_{\max.}$
114/16	26.7	0.520	0.3832	-0.00476	0.963	0.193	0.339	0.0907
114/15	25.9	0.453	0.3839	-0.00409		0.187		0.0947
106/14	22.7	0.614	0.3578	-0.00638	0.968	0.200	0.344	0.0804
106/16	25.7	0.481	0.3570	-0.00403		0.191		0.0882
106/15	28.2	0.414	0.3581	-0.00308		0.208		0.0808
108/13	12.14	0.405	0.1873	-0.00314	0.987	0.200	0.402	0.0465
108/11	33.2	0.543	0.1890	-0.00206		0.208		0.0455
108/12	25.5	0.577	0.1888	-0.00231		0.236		0.0387

A COMBINED HYDROGEN AND HELIUM LIQUEFIER

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ABSTRACT. A description is given of a helium liquefier which needs only liquid air for the initial cooling and is designed to enable low-temperature experiments to be made in the ordinary laboratory.

§ 1. INTRODUCTION

RECENT developments in low-temperature technique have made it possible to work at liquid-helium temperatures in any laboratory in which liquid hydrogen is available. However, as in many laboratories a supply of liquid hydrogen is unobtainable it seemed useful to design an apparatus in which only liquid air is required for the preliminary cooling and in which a small quantity of hydrogen, sufficient to obtain the necessary starting-temperature for the helium stage, is liquefied inside the apparatus itself. For occasional work it is simpler and much less expensive to construct a double liquefier of this type than to set up separate liquefiers for hydrogen and helium.

In the apparatus described here there is first a small Linde liquefier for hydrogen of the type described by Ruhemann⁽¹⁾. For the helium stage the expansion method developed by Simon⁽²⁾ is employed.*

The hydrogen liquefier is worked from high-pressure hydrogen cylinders so that no compressor is needed. For the helium liquefier a small compressor is used, but for occasional work this is not necessary as it would be quite possible to work with a high-pressure helium cylinder.

It was thought worth while to give a complete description of the apparatus and technique so that the important details in the construction and operation could be more easily reproduced.

§ 2. GENERAL DESCRIPTION OF THE APPARATUS

To illustrate the principle of the methods employed a simplified diagram of the liquefier is shown in figure 1 together with connexions to the hydrogen and helium circuits.

With the exception of the glass Dewar vessel *D* the apparatus is made entirely of metal and the various parts are soldered together.

* The possibility of constructing such a double liquefier was first shown by preliminary work by Kaishev⁽³⁾ in Prof. Simon's laboratory.

The liquid-hydrogen vessel *A* and the helium vessel *C* are suspended in an enclosure *E*₁ which is surrounded on the outside by liquid air contained in the Dewar vessel *D*. The temperature of the liquid air can be reduced below its normal boiling-point by pumping off through the outlet tube *q*. When the whole apparatus has reached the lowest temperature obtainable with liquid air, the enclosure *E*₁ is evacuated with a high vacuum pump.

High-pressure hydrogen enters the apparatus by the tube *a* and passes through the liquid air and the heat-exchangers to the expansion valve *V* where it ultimately liquefies, and the liquid drops into the vessel *A*. The outgoing gas passes out through the exchangers, so cooling the incoming gas. The gas leaves the apparatus by the tube *b* and passes ultimately through the flow-meter *F*₁ so that the rate of flow of gas can be measured.

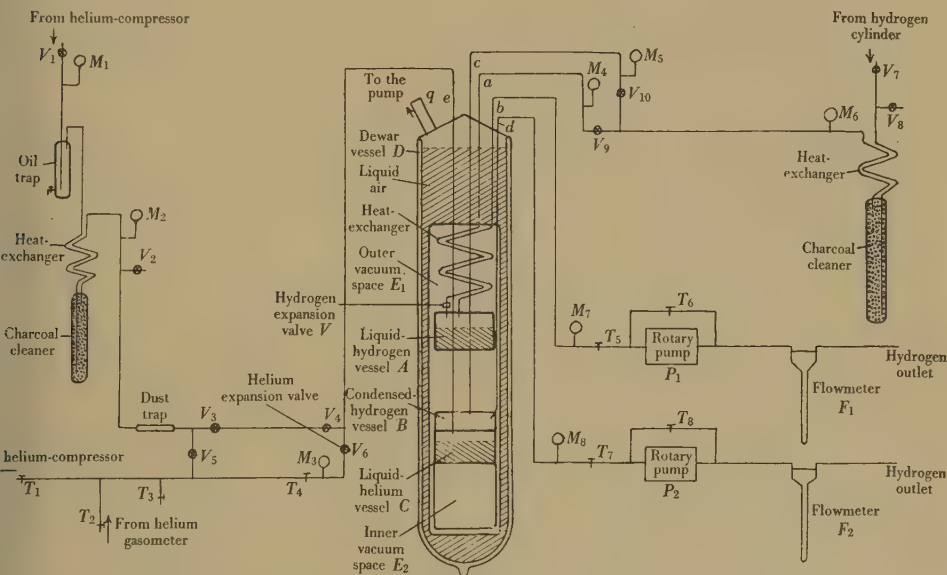


Figure 1. Simplified diagram of helium liquefier and external apparatus.

The vessel *C* is filled with helium gas maintained at a pressure of 130 atmospheres. In order to cool this gas further, liquid hydrogen is condensed in the vessel *B* by admitting hydrogen gas to the tube *c* so that it passes first through the liquid air and then through the liquid hydrogen in *A*, where it is condensed, and the liquid drops down into *B*.

When *B* is filled with liquid hydrogen at 20° K. the hydrogen inlet valve *V*₁₀ is closed and the temperature of *B* and *C* is further reduced by pumping off through the outlet tube *d* by means of the pump *P*₂. In this way the temperature can be lowered to about 11° K., below the triple point, 14° K. of hydrogen. During the whole of the cooling process, the helium vessel *C* is connected to the high-pressure helium supply. Ultimately nearly all the hydrogen in *B* is evaporated and contains helium at a pressure of 130 atmospheres and a temperature of 11° K.

The helium inlet valve V_4 is then shut and the valve V_6 is opened slowly so that the helium in C is expanded. This adiabatic expansion process gives rise to a considerable cooling, and eventually the helium liquefies in C . At the conclusion of the expansion, C is filled about two-thirds full with liquid helium at 4.2° K. The apparatus on which measurements are to be made is situated in the inner enclosure E_2 .

§ 3. COMPLETE DESCRIPTION OF THE APPARATUS

A complete diagram of the liquefier is given in figure 2, which is drawn to scale with the exception of the connecting tubes.

The apparatus is suspended from the upper brass cap J by the connecting tubes. The Dewar vessel D is joined to the cap by a rubber sleeve T with a packing of felt F between the metal and the glass. The Dewar vessel is filled with liquid air and can be pumped off through the tube q . Liquid air can be siphoned into the vessel from a storage flask through the tube m .

On account of the extremely low vaporization heat of liquid hydrogen and liquid helium (roughly $\frac{1}{10}$ and $\frac{1}{100}$ respectively of the value for oxygen per cm^3), it is essential to design the apparatus so that heat-conduction between parts at different temperatures is reduced to a minimum. Thus all connecting tubes are made of German silver and are as long and thin as possible.

The outer vacuum enclosure E_1 consists of the cylindrical copper case Y_1 soldered to the copper cap k_1 and similarly the inner vacuum enclosure consists of the case Y_2 soldered to the ring k_2 at the bottom of the helium vessel C . Surrounding the helium vessel C and the inner vacuum enclosure is the copper shield R which serves to prevent conduction of heat between the helium vessel and the outer case by the residual gas in the outer vacuum space. Direct heat-conduction between the parts at liquid-air temperature and the helium vessel must be entirely avoided, so all tubes must be in thermal contact with the hydrogen vessel A before proceeding to the helium vessel.

High-pressure hydrogen comes in by the copper tube a and passes through the inner tube of the exchanger X_1 through the copper spiral S_1 , immersed in liquid air, through the inner tube of the exchanger X_2 in the outer enclosure E_2 , and so to the expansion valve V . The expansion valve may be adjusted by means of the external handle H . On leaving the vessel A the cold hydrogen gas passes through the outer German-silver tube of the exchangers X_2 and X_1 , and when it leaves the apparatus by the tube b it is almost at room-temperature.

The inlet for the hydrogen which is to be condensed is at c . The gas is first cooled to liquid-air temperature in the copper spiral S_2 and then passes through the copper spiral S_3 in the liquid hydrogen vessel A , where it condenses and runs down into the vessel B . The vessel B is provided with the outlet tube d so that a flow of gas can be passed through B .

High-pressure helium is led in by the tube e and is cooled to liquid-air temperature in the copper spiral S_4 and to liquid-hydrogen temperature in S_5 . It then

passes through the German-silver spiral S_6 , and through the copper spiral S_7 in the condensed-hydrogen vessel, to the helium vessel C . The same tube also serves as the outlet tube.

To indicate approximately the temperature of the hydrogen-liquefier a small gas thermometer is employed. This is of the type used by Simon⁽²⁾ and consists of a brass vessel G_1 , with a volume of about 1 cm^3 , soldered to the top of the liquefier. It is connected by means of a capillary tube to a dial vacuum manometer. The thermometer is evacuated at room-temperature and filled with pure helium to a pressure of about 1 atmosphere. Change of temperature of G_1 gives rise to a change of pressure which is indicated on the manometer. The thermometer is conveniently calibrated at liquid-air temperature and the boiling-point and triple point of hydrogen, 20° and 14° K. respectively. A similar gas thermometer G_2 is used to indicate the temperature of the helium-liquefier.

For simplicity the specimen on which low-temperature measurements are to be made is shown in the diagram as a solid block K . The most satisfactory method of cooling the specimen is generally to use condensed helium which is contained in the vessel M . The helium is admitted at a pressure of 2 atmospheres (1 atmosphere over-pressure) *via* the tube n . It is cooled first to liquid-air temperature and then to hydrogen temperature, and on passing the helium-liquefier C it condenses and runs down through the thin-walled German-silver spiral S_8 into M .^{*} A shield prevents heat radiation from the external parts from reaching the specimen. If the thermal insulation of the specimen is good a temperature of 1° K. can be reached by pumping off the condensed helium.

§ 4. EXTERNAL APPARATUS

The helium necessary for the experiments is stored in an oil-filled gasometer. The pressures necessary for the experiments are obtained by using a small compressor. On coming from the compressor the helium is first passed through an oil-trap, figure 1, and is then purified by being passed through activated charcoal cooled in liquid air. To avoid waste of liquid air, the gas entering and leaving the cleaner passes through a heat-exchanger. The charcoal is contained in a thick-walled metal cylinder of volume 300 cm^3 . Before the starting of an experiment it is heated to about 300° C. and pumped off for several hours. After leaving the cleaner the gas passes through a dust-trap and then to the apparatus.

Hydrogen is contained in a cylinder of volume 50 litres at a pressure of 200 atmospheres[†] and is purified by passing through a charcoal cleaner of volume 1 litre. The flow-meters F_1 and F_2 consist simply of a capillary tube with a water manometer indicating the pressure-difference between the ends of the tube.

^{*} In figure 2 a capillary outlet tube o is shown coming from the helium condensation vessel M and passing up the central tube of the apparatus. It was included to assist the condensation of the liquid helium by allowing a small amount of gas to flow out during the condensation process. It has recently been found that its presence is probably not essential for the condensation.

[†] It is, however, quite possible to use the ordinary storage cylinders of volume 25 litres at pressure 120 atmospheres.

The glass apparatus is not shown in the diagram. It consists of two mercury condensation pumps for pumping the vacuum spaces and the condensed helium, with liquid-air traps and discharge tubes. The pumps are heated by electric furnaces as it is of course very undesirable to have flames near an apparatus using hydrogen. There are two flasks of volume 3 and 5 litres respectively which can be exhausted by the pumps and filled with pure helium from the helium circuit. This helium is admitted to the vacuum spaces to give thermal exchange when desired, and is used also as a supply of helium for condensation in the vessel *M*. There is also a mercury manometer for measuring the vapour pressure of the helium condensed in *M*.

§ 5. DIMENSIONS OF THE APPARATUS AND CONSTRUCTIONAL DETAILS

As it is impossible to show the dimensions completely in a diagram the more important details are given here. The hydrogen vessel *A* is turned from solid copper and has a wall thickness of 2 mm. The spirals *S*₃ and *S*₅ are of copper tube having an external diameter of $\frac{3}{16}$ in. and a wall thickness of $\frac{1}{32}$ in. After the spirals have been mounted in the vessel *A* the flat annular top is placed in position and silver-soldered in. The volume of the vessel is 75 cm³. The helium vessel *C* is turned from solid phosphor-bronze, though copper could be used equally well. The external walls have a thickness of 4 mm. and the internal walls 2 mm. The annular top is silver-soldered in. The spiral *S*₇ is of $\frac{3}{16}$ -in. copper tube. The vessel *B* is beaten out of copper sheet and soft-soldered to *C*. Further details of the tubes are given in the following table:

Tube	Material	External diameter	Wall-thickness
<i>f</i>	German silver	1 cm.	0.1 mm.
<i>S</i> ₆	" "	4 mm.	0.5 mm.
<i>S</i> ₂	Copper	$\frac{3}{16}$ in.	$\frac{1}{32}$ in.
<i>S</i> ₄	"	$\frac{1}{4}$ in.	$\frac{1}{32}$ in.
<i>S</i> ₁	"	2.5 mm.	0.5 mm.
<i>S</i> ₃	German silver	2.0 mm.	0.1 mm.
<i>e</i>	" "	4 mm.	0.5 mm.
<i>d</i> *	" "	4 mm.	0.2 mm.
<i>n</i> †	" "	4 mm.	0.2 mm.
<i>c</i>	" "	2 mm.	0.2 mm.
<i>b</i>	" "	8 mm.	0.1 mm.
<i>G</i> ₁ , <i>G</i> ₂	" "	0.7 mm.	0.2 mm.
<i>X</i> ₁ ‡	" "	5 mm.	0.5 mm.
<i>X</i> ₂ ‡	" "	4 mm.	0.3 mm.

* The portion of *d* adjacent to the hydrogen vessel *A* is of $\frac{3}{16}$ -in. copper tubing and is soldered to *A*.

† The portions of *n* passing the vessels *A* and *C* and soldered thereto are of $\frac{3}{16}$ -in. copper tubing.

‡ The internal tubes of *X*₁ and *X*₂ are of copper, diameter 2.5 mm. and wall-thickness 0.5 mm.

The exchangers are constructed by placing one tube inside the other and then winding the two tubes into the spiral form. The valve *V* is turned from solid brass and the spindle is of solid steel of diameter 3 mm. The outer tube *h* which has to

support the high pressure is of German silver with a diameter of 6 mm. and wall-thickness of 1.0 mm. The construction of the valve at the upper end of the spindle is similar to that of the ordinary high-pressure valve. The valve is made tight with a packing consisting of a mixture of graphite and lead. In the external hydrogen and helium circuits the tubes used for the high pressure are of copper, with a diameter of $\frac{1}{4}$ in. or $\frac{3}{16}$ in. and a wall-thickness of $\frac{1}{32}$ in. For the low-pressure circuit, tubes of composition alloy having an internal diameter of $\frac{1}{2}$ in. are employed.

In the construction of the apparatus each part is tested in turn for strength and absence of leaks with hydrogen gas at suitable pressure.

When the vessels *A* and *B* have been constructed and tested they are mounted on the central tube *f*, the caps *k* and *J* are assembled on the tube, and the connecting tubes and spirals are then soldered in position. Soft solder has been used for nearly all the joints.

When the apparatus has been completed it is rigidly clamped by the upper cap *J* and the various connexions are made to the hydrogen circuit, the helium circuit and the glass apparatus. The upper end of the central tube *f* is closed with a glass tube *p*. All glass-metal joints are made with vacuum wax and all such joints are kept as far away as possible from the liquefier so that they may not crack during the cooling of the liquefier.

The case Y_2 of the enclosure E_2 is soldered to the ring k_2 with Wood's metal, and similarly the screen *R* is soldered to the hydrogen vessel *A*, and the case Y_1 is soldered to the cap k_1 , Wood's metal being used. When changes have to be made in the experimental apparatus in the enclosure E_2 it is only necessary to unsolder these three Wood's-metal joints.

As copper sheet is often not vacuum-tight, all large metal surfaces, such as the vacuum cases Y_1 and Y_2 , are covered with a thin layer of tin solder.

§ 6. OPERATION OF THE LIQUEFIER

A description is given here of the operation of the liquefier during a typical experiment. When the hydrogen and helium cleaners have been heated and pumped out for 1 or 2 hours they are cooled in liquid air and filled with compressed hydrogen and helium respectively. The hydrogen vessels *A* and *B* in the liquefier are pumped out and filled with pure hydrogen to a pressure of 2 or 3 atmospheres. The helium vessel *C* is pumped out and filled with compressed helium. The vacuum spaces E_1 and E_2 and the helium condensation space *M* are exhausted. The glass apparatus is pumped out and the 5-litre flask is filled with pure helium to a pressure of 2 atmospheres. The readings of the gas thermometers are taken. The cooling is now started and the following sequence of operations is carried out.

0 hr. The Dewar vessel *D* containing liquid air* is put on the apparatus. Helium gas is now admitted to the enclosures E_1 and E_2 to a pressure of about 1 cm. This gives thermal exchange between the inner parts and the outer case.

0 hr. 40 min. The Dewar vessel is pumped.

* Liquid oxygen is generally used in this laboratory, but liquid air or nitrogen would be preferable if they were available.

1 hr. 15 min. The whole apparatus is now at 70° K. The outer vacuum space is pumped to high vacuum.

1 hr. 20 min. The expansion valve is opened and the hydrogen flow is started. The pressure of hydrogen used is 150 atmospheres. The valve is adjusted to give a flow of 70 litres per minute. The temperature falls rapidly.

1 hr. 24 min. Hydrogen begins to liquefy at the valve. Vessel *A* is now at 70° K. The hydrogen flow is reduced to 30 litres per minute as with a greater flow exchanges are inefficient. From time to time liquid air is admitted to the Dewar vessel through the siphon. The level is always kept near the top of the Dewar vessel.

1 hr. 34 min. Regular oscillations on the flow-meter F_1 show that the vessel *A* is full of liquid. The cooling of the vessels *B* and *C* is now started by admitting hydrogen at a pressure of about 3 atmospheres to the vessel *B*. The hydrogen condenses in passing the vessel *A* and the liquid falls into *B* and evaporates again. The cooling is assisted if the outlet tap T_7 of *B* is partly opened so that there is a flow of about 2 litres per minute through the vessel. When the temperature is about 40° K. the tap T_7 is closed.

1 hr. 43 min. The temperature of *B* has now reached 20° K. and liquid begins to collect in *B*, the pressure being kept at 3 atmospheres by adjusting the inlet valve V_{10} . Helium is slowly compressed into the vessel *C*.

1 hr. 54 min. The vessel *B* is now full of liquid. This is shown by the fact that when the inlet valve V_{10} is closed completely the pressure remains at 3 atmospheres. Helium is still slowly compressed into *C* and the liquefaction of hydrogen in *A* is continued until the hydrogen-liquefier *A* is full, and the liquefaction is then stopped. The helium pressure is now 130 atmospheres.

2 hr. 10 min. The pumping off of the condensed hydrogen by the rotary pump is started.

2 hr. 16 min. The hydrogen in *B* has reached the triple point 14° K. The pumping of the hydrogen vessel *A* is started using the pump P_2 .

2 hr. 30 min. Hydrogen liquefaction in *A* is restarted.

2 hr. 40 min. *A* is full of liquid and the flow is stopped.

3 hr. 5 min. Nearly all the hydrogen in *B* has now been pumped away and the temperature is about 11° K. The helium pressure is 120 atmospheres. The inner enclosure E_2 is evacuated. The helium is now ready for expansion. The helium inlet valve V_4 is closed and the helium condensation vessel *M* is connected with the outer flask. The helium outlet valve V_6 is slowly opened so that the expansion of helium in *C* is started. During the expansion the taps T_5 and T_7 on the outlet of the vessels *A* and *B* are closed.

3 hr. 14 min. The expansion ends. The vessel *C* now contains liquid helium at 4° K. The tap T_5 is opened again.

3 hr. 17 min. 1.5 litres of helium gas have been condensed in *M*. This is about 100 cm.³ of liquid helium but is sufficient for cooling the average experimental specimen. It would cool 50 kg. of copper from 4° to 1° K. The pumping of the helium in *M* with the high vacuum pump is now begun.

3 hr. 22 min. The vessel *M* and the specimen *K* have now reached a steady temperature of 1.3° K. and the low-temperature measurements can begin. The temperature is indicated by the vapour pressure of 1.5 mm. which is read on the mercury manometer.

4 hr. 10 min. The helium liquefier is now empty and begins to warm slowly.

It is convenient and economical to make several expansions in succession. At 5 hr. 40 min. a second expansion and at 8 hr. 10 min. a third expansion could be made. At each expansion the liquid helium in *C* generally lasts for 1 or 2 hours, depending on the amount of helium which has been condensed in *M*,* and this is sufficient for most experiments. If it were desired to make experiments for longer times than this it would only be necessary to increase the size of the vessel *C* so that a greater quantity of liquid could be obtained. The size of the vessels *A* and *B* would have to be increased in proportion. It is important that the ratio of the sizes of *B* and *C* shall be calculated correctly so that the correct amount of hydrogen for cooling the helium in *C* may be contained in *B*.

It is not always necessary to use condensed helium for cooling the specimen *K*; indeed, for many electrical or magnetic experiments it is sufficient to fix the specimen in thermal contact with the helium vessel *C* and the temperature can be lowered if necessary to 2° K. by pumping out this vessel. With this arrangement it is not necessary to have even an inner vacuum enclosure.

Sometimes it is more convenient to suspend the specimen in the inner enclosure and to cool it with exchange gas or, of course, the specimen can be enclosed in a copper or glass vessel and cooled in that way. Cooling with exchange gas is not very satisfactory if calorimetric experiments are to be made, as the gas has to be completely pumped away before the experiment is started and this may take a considerable time.

For three expansions the total quantity of liquid air required for the liquefier and the cleaners is about 16 litres, and 6 cubic metres of hydrogen are needed. The greater part of the liquid air (9 litres) is used for the cleaners.

Improvement in the performance of the liquefier could have been obtained by increasing the total length of the apparatus so as to increase the length of the connecting tubes and thus reduce the rate of evaporation of liquid hydrogen and helium.

When once the initial difficulty of handling the apparatus had been overcome it was found possible to make low-temperature experiments regularly and satisfactorily with this liquefier, and calorimetric measurements have recently been made with it on liquid and solid helium. These will be described in a later publication.

* For every cm^3 condensed in *M* about 4 cm^3 of liquid are evaporated from the liquefier *C*. The additional 3 cm^3 represents the amount necessary to cool the incoming gas.

§ 7. ACKNOWLEDGMENTS

In conclusion I should like to express my thanks to Prof. Simon, who suggested construction of this liquefier and has given me very valuable advice and assistance, and to Prof. Lindemann for his interest in the work and for extending to me facilities of the Clarendon Laboratory. I would like especially to thank Dr. P. T. P. for his advice on the construction of the liquefier and his help with the experiments. The work has been assisted by the receipt of a research grant from the Department of Scientific and Industrial Research.

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ABSORPTION SPECTRA OF THE CHLORIDES AND OXYCHLORIDES OF SULPHUR

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ABSTRACT. The absorption spectra of the vapours of SCl_2 , S_2Cl_2 , SOCl_2 and SO_2Cl_2 have been investigated in the visible and ultraviolet regions, and the continuous absorptions observed are correlated with photodissociation processes.

§ 1. INTRODUCTION

THE absorption spectra of these substances have been measured in the liquid state^(1,2). The measurements do not, however, enable one to correlate the energies of dissociation with the regions of selective absorption, for two reasons: (i) it cannot be ascertained whether the maxima are envelopes of a band system or represent true maxima of continuous absorption due to photodissociation; and (ii) the long-wave-length limit of absorption, a knowledge of which is necessary for an understanding of the process of photodissociation, gives too small an energy value, owing, no doubt, to the great number of molecules in higher vibrational levels of the ground state⁽³⁾. These difficulties can to a great extent be minimized by studying the absorption of the substances in the state of vapour, and such an investigation has accordingly been undertaken. Preliminary reports of the work have already been published⁽⁴⁾.

§ 2. EXPERIMENTAL

The substances were contained in a side bulb attached to the main apparatus consisting of the absorption cell of fused silica and the usual vacuum arrangement with a manometer. The vapour was introduced into the absorption cell after the apparatus had been exhausted, the apparatus being thoroughly washed many times before the final sample of vapour was taken. For work in the ultraviolet, absorption cells of lengths 5, 10 and 20 cm. were used with a hydrogen tube for the source of continuous spectrum and a quartz spectrograph of medium dispersion. Copper arc lines were utilized for standard wave-lengths. For the visible region a glass tube of length 100 cm., to the ends of which were sealed plane glass windows, was used as the absorption cell; the continuous source was a gas-filled 8-volt bulb

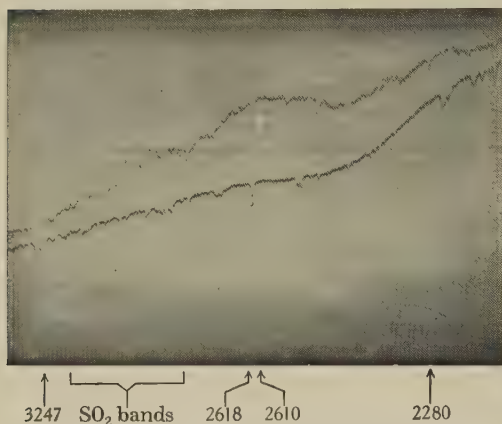


Figure 1. SCl_2 (ultraviolet).

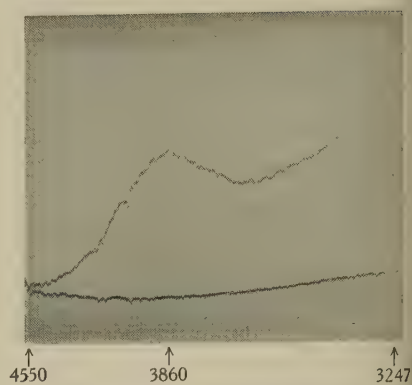


Figure 2. SCl_2 (violet).

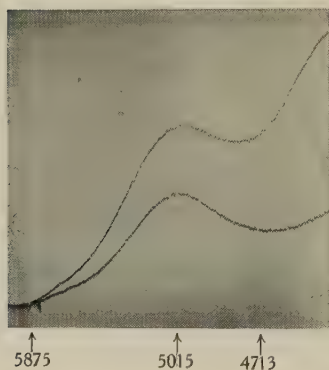


Figure 3. SCl_2 (green).

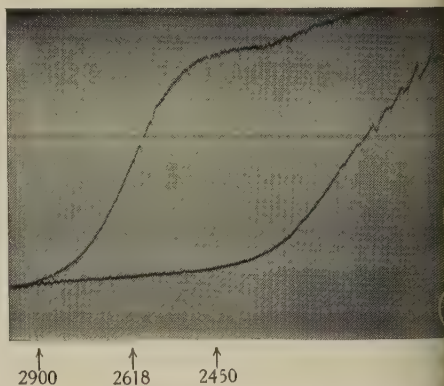


Figure 4. SOCl_2 .

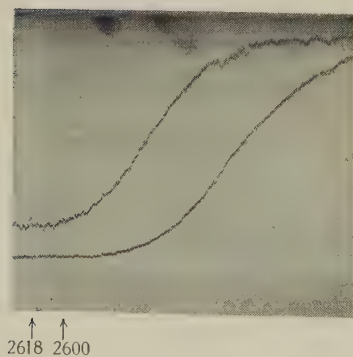


Figure 5. SO_2Cl_2 .

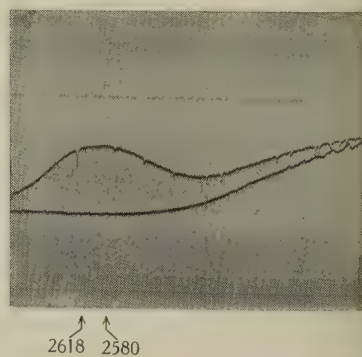


Figure 6. S_2Cl_2 .

In each figure the lower curve represents the light source and the upper curve indicates the absorption.

ing a straight filament which during the exposure-time was run on a constant age of 10. The resolving instrument was a Hilger constant-deviation glass spectrograph. The necessary standard lines were given by the helium-plus-mercury charge tube. The plates were measured on the recording photometer; the long-wave-length limits and the positions of the maxima of absorption were determined on the microphotometer plates. All the substances have a great tendency to emit SO_2 bands in absorption, but this tendency was minimized by careful and repeated washing of the apparatus with the vapour, distillation of the liquids in vacuum, and the use of glass needle valves after Bodenstein⁽⁵⁾. Some of the spectra, especially those for SCl_2 , showed bands which did not completely agree in appearance with the well-known absorption bands of SO_2 . Actual measurement and analysis, however, have convinced us that all these bands, some of which have previously been classified, are to be attributed to SO_2 ; and the results of the analysis will be recorded in a separate communication.

§ 3. RESULTS AND DISCUSSION

The absorption by sulphur dichloride is continuous and exhibits three maxima, which will be seen in the microphotometer plates, figures 1 to 3, and in the diagram, figure 7. Starting from the short-wave side, we find the first absorption region about 90 Å. from λ 2350 to λ 2260 with a maximum at λ 2280. The second region occupies about 320 Å. from λ 2770 to λ 2450, with a maximum at λ 2610. The beginning of the third absorption appears to be at λ 4550 on a Wellington anti-iron plate in the quartz spectrograph, but at λ 5825, with a definite inflection at λ 5165, on a panchromatic plate in the glass spectrograph; this absorption has a maximum at λ 3860 and ends at λ 3700. It is found⁽⁶⁾ that Cl_2O shows two corresponding maxima, one due to the photodissociation into $\text{ClO} + \text{Cl}$, the other into $(\text{O})^* + \text{Cl}$, the energy-difference between the two being 2800 cm^{-1} . The energy of excitation of SCl should be slightly less than this value. The difference between λ 5825 and λ 5165, which is 2193 cm^{-1} , may therefore roughly represent the difference between the two long-wave limits of the photodissociation processes corresponding to those of Cl_2O mentioned above. Since, however, real maxima could not be found, and the absorption curves of many substances show a lengthening on the long-wave side, due evidently to losses by reflection very similar in appearance to the curve in figure 7, we prefer to take λ 5165 as the real long-wave limit of the process of photodissociation of the SCl_2 molecules ($\text{SCl}_2 \rightarrow \text{SCl} + \text{Cl}$). Even if λ 5825, and not λ 5165, represents the energy of the photodissociation, the difference, 2193 cm^{-1} , is well within errors of computation.

Thionyl chloride, SOCl_2 , figure 4, shows one region of absorption of width about 500 Å., from λ 2900 to λ 2400, with a maximum at λ 2450. Sulphuryl chloride, SO_2Cl_2 , figure 5, gives one continuous absorption starting from 2600 Å., with no maximum within the limit of the quartz region. Sulphur monochloride, S_2Cl_2 , figure 6, has an absorption region of 380 Å. from λ 2770 to λ 2390 with a maximum at λ 2580. The data are collected in table 1.

All these regions of continuous absorption are due to transitions from the normal states of the molecules to various excited repulsive states. The breadth of the absorption region is a measure of the steepness of the repulsive curve. This steepness increases from SCl_2 to SO_2Cl_2 in the order given in the table. With the exception of SO_2Cl_2 , where the region of absorption appears to be very extensive, the repulsive curves are relatively flat and the agreement between the computed

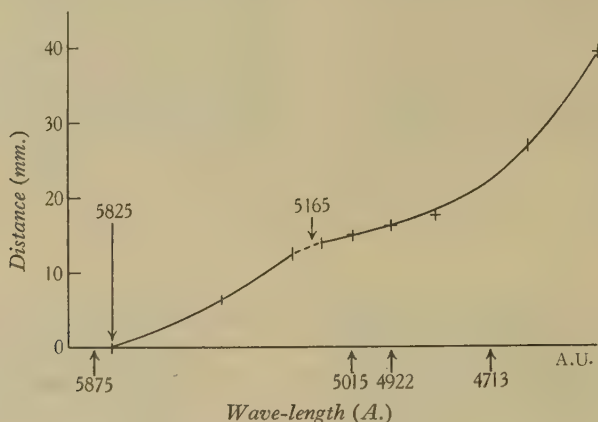


Figure 7. Showing the distance between two curves of figure 3, for SCl_2 .

energy of dissociation and the long-wave limit clearly indicates that the photolytic processes involved produce unexcited dissociation products, with the exception of the absorption at λ 2350 in the case of SCl_2 . Similar agreement obtains also for SO_2Cl_2 , which shows that although the repulsive curve is relatively steep the products of dissociation are unexcited. The observed maxima represent the most probable values of the kinetic energy of the products of dissociation, indicated by the relative positions of the curves in the Franck-Condon diagram.

Table 1. Wave-lengths (A.) of the beginning *a*, maxima *b*, and ends *c* of the absorption regions. Figures in parentheses are the corresponding numbers of kcal./mol.

	I		II			III			IV		
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
SCl_2	5825 (48.5)	5165 (55.4)	4550 (62.4)	3860	3700	2770 (104)	2610	2450	2350 (122.4)	2280	2260
S_2Cl_2						2770 (104)	2580	2390			
SOCl_2						2900 (97)	2450	2400			
SO_2Cl_2									2600 continuous \rightarrow (108.6)		

The thermochemical values given in table 2 represent the heat of formation of the constituent atoms in the gaseous state and are obtained in the usual way from the data given by the Landolt-Börnstein Tables. For the energy of dissociation of S_2 we do not use the value 102.6 kcal./mol. determined⁽⁷⁾ by predissociation in the spectrum of S_2 ,* but prefer to calculate it from the point of convergence of the absorption bands ($B^3\Sigma \leftarrow X^3\Sigma$) which has been directly observed⁽⁸⁾ at $100 \pm 1000 \text{ cm}^{-1}$. Deducting from this the energy, 9240 cm^{-1} , of excitation of the state of sulphur⁽⁹⁾ we obtain $30,760 \pm 1000 \text{ cm}^{-1}$ or about 90 kcal./mol. as the energy of dissociation of S_2 into two unexcited S atoms.†

Table 2

$\text{S} + 2\text{O}$	$=\text{SO}_2$	+ 248 kcal./mol.
$\text{S} + 2\text{Cl}$	$=\text{SCl}_2$	+ 123 „
$\text{S} + \text{O} + 2\text{Cl}$	$=\text{SOCl}_2$	+ 215 „
$2\text{S} + 2\text{Cl}$	$=\text{S}_2\text{Cl}_2$	+ 185 „
$\text{S} + 2\text{O} + 2\text{Cl}$	$=\text{SO}_2\text{Cl}_2$	+ 317 „
$\text{S} + 3\text{O}$	$=\text{SO}_3$	+ 330 „

The value for SCl_2 appears to be slightly less reliable.

The long-wave-length limit of SO_2Cl_2 gives 108.6 kcal./mol. and the difference between the heats of formation of SO_2Cl_2 and SOCl_2 is 102 kcal./mol. Since it is not possible to follow the long-wave-length limit right up to the point where the products of dissociation have zero kinetic energy, the agreement is very good. So the absorption at $\lambda 2600$ represents the dissociation of SO_2Cl_2 into unexcited SO_2 and O . The maximum of absorption is evidently below the quartz region and is in a different position from that of the other substances.

All the other substances exhibit a common absorption in the region between $\lambda 2000$ and $\lambda 2900$. It is not possible to explain away this common absorption as due to a common impurity; this is clearly shown by the absorption curves for the excited state, where the maximum for each substance represents a higher value of absorption coefficient than could be yielded by an impurity. Again, it is unreasonable to attribute the common absorption to different processes of photo-dissociation in different molecules. It is true that the positions of the maxima and long-wave limits are not exactly identical, but the differences are clearly due to the fact that, as we now know, the law of additivity in the case of bond energies is good only in zeroth approximation⁽¹⁰⁾, and already the differences in the attractive forces in the different molecules spoil the exact operation of this law. This absorption has to be taken as characteristic for each molecule. Since only the Cl linkage is common to all these molecules, it is this that is involved in this absorption. Further, for the following reasons, this continuous absorption must be due to the splitting off of the Cl atoms. The long-wave limits of the maxima are directly values of about 104 kcal./mol. for S_2Cl_2 and 97 kcal./mol. for

Linear extrapolation of the vibrational levels of the S_2 molecule will give too high a value for dissociation energy on account of the existence of perturbations in a number of these levels. Dissociation data also naturally yield values that are too high.

This point is discussed in greater detail in a forthcoming paper by one of us.

SOCl_2 . If only one Cl were split off, the removal of the second Cl would further involve nearly the same energy-change, if not a slightly greater one on account of the repulsion of the two Cl atoms. On this basis, therefore, about 200 kcal./mol. would be used up for the two SCl bonds; and since the atomic heats of formation for SOCl_2 and S_2Cl_2 are 215 and 185 kcal./mol., only about 15 kcal./mol. would be left over for the S=O bond and none at all for the S=S bond. This is obviously impossible. If, however, we deduct 97 kcal./mol. from the energy of formation of SOCl_2 , and 104 kcal./mol. from that of S_2Cl_2 , there remain 118 kcal./mol. for the double bond in SO and 88 kcal./mol. for the double bond in S_2 . From band-spectrum data we obtain, for the SO bond, 117.6 kcal./mol. for the ground state of $\text{SO}^{(1)}$, and 90 kcal./mol. for the S_2 bond as was shown above. The agreement is very good. We have further evidence in favour of this view. This difference of 102 kcal./mol. between the energies of formation of SO_2Cl_2 and SOCl_2 indicates that the energy of this double bond in the diatomic molecule still prevails as true bond energy in the polyatomic molecule, modified rather than changed by the difference in the forces of repulsion. This is so because the electronic configuration of a diatomic molecule of the type SO, S_2 , etc. need not suffer any change when the molecule becomes polyatomic, the diatomic molecule already possessing two free valencies in the $^3\Sigma$ ground state. Again, half the atomic heat of formation of SO_2 , namely 124 kcal./mol., is about equal to the above value of 118 kcal./mol. for the double bond in SO. But the difference of 88 kcal./mol. between the energies of formation of SO_2 and SO_3 gives a considerably smaller value for the third bond in SO_3 . In any case it is clear that the common absorption region certainly corresponds to the splitting off of both the chlorine atoms in these molecules.

This view is further corroborated by the absorption spectrum of SCl_2 . In this case the absorption on the long-wave side corresponds to the splitting off of one Cl atom, and the second one, therefore, to the splitting off of the second Cl in addition to the first. As there are only two bonds, no other explanation is possible if the common absorption is to be properly correlated. Indeed the value 55.4 kcal./mol., which is obtained from the long-wave limit λ 5165, is near to half the total energy of formation of SCl_2 , namely 61.5 kcal./mol. The value 123 kcal./mol. is, as has already been stated, a rough one, for here the original measurements from which it is derived are obtained by indirect experiments which in reality give the heat formation of SCl_2 in solution with S_2Cl_2 . The long-wave limit at λ 2770, i.e. about 104 kcal./mol., represents the splitting off of the second Cl atom also.

The absorption beginning at λ 2350 has to be correlated with the dissociation into at least one excited product. The repulsive curve in this case is very flat, because the width of the region is small and, therefore, indicates that it does not run down to the ground level of the separated system of unexcited products. The energy-difference of the two long-wave limits, λ 2350 and λ 2770, is 6450 cm^{-1} . We correlate this region of absorption to the process of dissociation of SCl_2 into $2\text{Cl} + \text{S}(^1\text{D})$. The energy of excitation of this ^1D state is about 9240 cm^{-1} . The agreement is not satisfactory, but better agreement is rather difficult to expect in view of the facts that the two repulsive curves obviously do not run parallel, that

long-wave limit is never well defined, and that the difference in energy which is sought is in itself small.

§ 4. OPTICAL VALUES OF BOND ENERGIES

The values of the bond energies derived from optical measurements here and elsewhere are given in table 3.

Table 3

Number of bonds	Designation of bonds	Derivation of bonds	Bond energy kcal./mol.
Two	S—Cl	S ₂ Cl ₂	104
Two	S—Cl	SOCl ₂	97
Two	S—Cl	SCl ₂	104
One	S—Cl	SCl	55·4
One	S=O	SOCl ₂	118
One	S=O	SO*	117·6
One	S=O	SO ₂ Cl ₂	108·6
One	S=S	S ₂ Cl ₂	88
One	S=S	S ₂ *	90

* Taken from band-spectrum data.

On account of the forces of repulsion, the energy of the SCl bond should indeed be lower in SOCl₂ than in S₂Cl₂, and lower for the second than for the first bond in S₂Cl₂; and the energy of the SO bond should be lower in SO₂Cl₂ than in SOCl₂.

§ 5. CONCLUSIONS

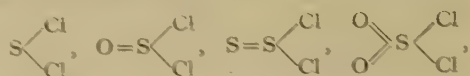
The following observations upon the work which has been described will perhaps not be out of place.

(i) The first process of dissociation of SO₂Cl₂ concerns the splitting off of an O atom, not a Cl atom in spite of the fact that the double bond of O represents a higher energy than that of the single bond of Cl. This is probably so because the oxidation of SOCl₂ into SO₂Cl₂ involves the activation of the two original *s* electrons of sulphur which still form a repulsive group in the tetravalent sulphur. Therefore this is the energy loss which occurs to SO₂Cl₂. The low value of the third SO bond in SO₃ might be connected with this phenomenon. As in CO₂⁽¹²⁾, the ground state of the paramagnetic SO₃ molecule does not originate from O (³P) plus the ground state of diamagnetic SO₂, but from an excited term of SO₂.

(ii) The energies per bond remain rather constant in all these molecules.

(iii) In SCl₂ we observe two different processes of photodissociation whereby the first link and then the second link undergoes fission, as in Cl₂O. In SOCl₂ and S₂Cl₂, in which all the four *p* electrons of S share in the linkage, the first photochemical process breaks up both SCl links. A process in which only one Cl atom is split off does not occur, or rather occurs with such low probability that the corresponding absorption cannot be found; otherwise these substances would be strongly coloured like SCl₂.

(iv) We have assumed in this paper that the structure of the molecules corresponds to the classical formulae such as



each bond representing a pair of electrons, one belonging to each atom. Other formulae implying semipolar double bonds and singlet linkages have been based on the measurements of the parachors of these substances, but recently it has been shown⁽¹³⁾ that molecular parachors do not provide diagnostic information with regard to the nature of the linkage in such cases. On the other hand, the Raman effect establishes⁽¹⁴⁾ the validity of the above chemical formulae, and the fact that the bond energies remain nearly unaltered in these molecules, as has been shown above, as well as in related ones like SO, S₂, SO₂, etc., is entirely consonant with this view.

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THE INTEGRATION OF THE GLARE EFFECTS FROM A NUMBER OF GLARE SOURCES

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ABSTRACT. The effect of a number of glare sources on indirect vision, 5° above the horizon, is shown to be equal to the sum of their separate effects, the criterion of equality being that the equivalent background brightness of all the sources measured together is the same as the sum of the equivalent background brightnesses measured separately.

§ 1. INTRODUCTION

It has been shown by Holladay and by Stiles⁽¹⁾ that the effect of a glare source in the field of view of an observer upon the brightness difference threshold is equivalent to that of a uniform background of a certain brightness given by

$$\beta = \frac{kE}{\theta^n} + B \quad \dots\dots(1),$$

where β is the equivalent background brightness, E is the illumination at the eye of the observer due to the glare source, θ is the angle subtended at the eye between the source and threshold test area, B is the actual background brightness and k and n are constants. k and n have approximately the values 10 and 2 respectively. Holladay further showed that, if a number of glare sources were visible in the field of view, the total effect was equivalent to a background brightness given by

$$\beta = k \left(\frac{E_1}{\theta_1^n} + \frac{E_2}{\theta_2^n} + \dots + \frac{E_p}{\theta_p^n} \right) \quad \dots\dots(2),$$

where suffixes 1, 2 ... p refer to the several glare sources. Holladay's work on these subjects was done with a test spot of maximum diameter 0.47° centred at the fovea of the observer's eye. The type of vision concerned was therefore purely foveal. A larger test spot, even though centred at the fovea, may give results showing a mixture of foveal and parafoveal types of vision.

In the extension of the equivalent background brightness formula to the general case, in which the test spot may fall on retinal areas other than the fovea, one of the steps is to show that the summation expressed in equation (2) is valid for all retinal areas. In the present communication this is demonstrated for a small test area on the retina 5° above the fovea. Distance and direction relate to the external field of view.

§ 2. EXPERIMENTAL CONDITIONS

The following arrays of glare sources were used. (a) A circle of twelve equally spaced glare sources centred at the test spot and of radius 3.05° . The glare sources were small 4-volt 2-watt lamps, the current through each being adjusted so that the candle powers were very nearly equal. (b) A circle of glare sources similar to

(a) but of diameter 14.6° . (c) Twelve glare sources arranged in a spiral of one turn, the distances of the sources from the test spot increasing from 1.03 to 19.7° in a geometric series. Each glare source was adjusted in intensity so that it gave approximately the same equivalent background brightness at the test spot. That is, the intensity of each glare source was inversely proportional to the square of its angular distance from the test spot.

In all cases the background brightness under glare conditions was zero.

§ 3. EXPERIMENTAL PROCEDURE

With each of these arrays of glare sources the equivalent background brightness of the sources was measured separately, and then the equivalent background of the whole array was determined. The latter value should equal the sum of the individual equivalent backgrounds if the summation law holds.

The determination of an equivalent background involves a measurement of threshold under the glare conditions and a measurement of the background brightness giving the same threshold. The latter is most easily obtained from a curve of threshold against background brightness. To supply these data, readings were taken according to the following plan: (a) one threshold reading for each glare source taken separately in a random order; (b) six threshold readings for the whole array of glare sources; (c) six threshold readings for each of a series of four or five background brightnesses covering the necessary range; (d) a repetition of (b).

All threshold readings for this work were taken with the brightness difference threshold meter described by Crawford and Stiles⁽²⁾. The test spot in this instrument is exposed for a short flash of duration $1/400$ second; its diameter is approximately 0.05° .

§ 4. RESULTS

The table shows the results obtained.

Table I

Glare-source array	Observer	Sum of equivalent backgrounds for each lamp measured separately (candle/ft ²)	Equivalent background for all lamps measured together (candle/ft ²)	Difference per cent
(a)	B. H. C.	.103	.100	+ 3
(a)	F. W. C.	.137	.100	+ 37
(b)	B. H. C.	.036	.047	- 23
(b)	F. W. C.	.046	.039	+ 18
(c)	B. H. C.	.027	.027	0
(c)	F. W. C.	.019	.035	- 17
(c)	F. W. C.	.026	.028	- 7
(c)	(second series) C. D.	.030	.027	+ 11
			Mean difference	+ 3
			Mean error	± 15

These results may be taken to demonstrate the approximate validity of the additive law. Each pair of figures given is the result of two to three complete runs taken within a few days of each other. It would appear that an observer may sometimes show a consistent difference between equivalent background brightnesses determined separately and collectively, but on the average of all the results the difference is negligible.

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STILES, W. S. *Proc. roy. Soc. B*, **104**, 322 (1929).
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THE DISCRIMINATION OF THE SATURATION OF COLOURS

By F. L. WARBURTON, A.R.C.S., D.I.C., M.Sc., A.Inst.P.

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ABSTRACT. Recent data on the sensitivity to saturation-differences have been correlated with the complementary colour-mixture data for the same observer. The experimental results are discussed on the basis of the three-component theory of Young and Helmholtz, and an attempt has been made to explain them by applying Weber's law to the component colours of the theory.

§ 1. INTRODUCTION

IN a paper presented at the Physical Society's discussion on vision⁽¹⁾ jointly by Dr L. C. Martin, Mr W. J. Morgan and the author, a preliminary account was given of some experimental work on the sensitivity of the eye to differences in the saturation of colours. The work has since been completed by the same workers and a full experimental account has been published by the Medical Research Council in their Special Report Series⁽²⁾. In neither of these papers has more than a brief account been given of the theoretical aspects of the work. In the present paper the results are discussed on the basis of the Young-Helmholtz theory.

In investigating the sensitivity of the eye to saturation-differences two main methods of approach were adopted. In the first the total number of perceptible steps between each of a number of pure spectral colours and white was determined, either by adding the colour to white step by step until the mixture contained only spectral light, or *vice versa*. In this way the colorimetric purity of each step can be obtained as follows. If L_C is the luminosity of the colour,

$$L_C = L_S + L_W,$$

where L_S is the luminosity of the spectral component and L_W that of the white.

Then the colorimetric purity $p = L_S/L_C$. This method gives a fairly accurate measure of the total number of steps between each spectral colour and white, and a somewhat less accurate measure of the variation in the size of the purity-discrimination limen Δp with colorimetric purity. The relation between the total number of steps and the wave-length is shown in figure 1.

In the second method the colorimetric purity of the colour just discriminable from white for each hue has been determined with a considerable degree of accuracy by making a large number of successive determinations. The results have been given by plotting L'_C/L_S for this colour against the wave-length λ , figures 2 and 3.

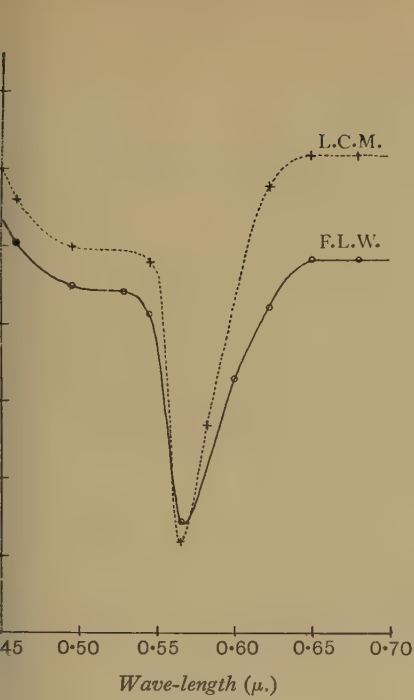


Figure 1.*

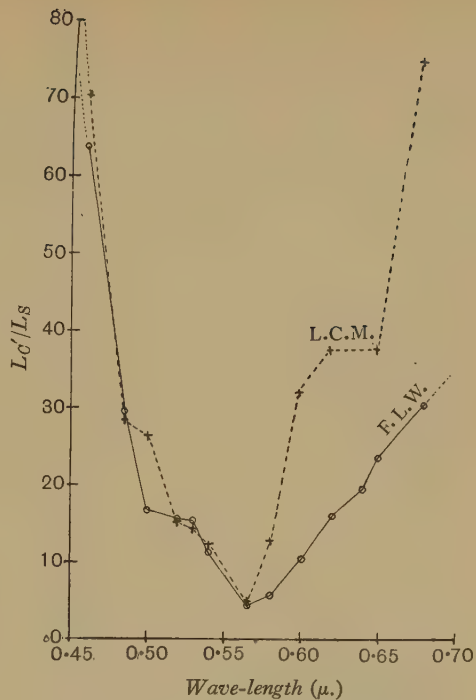


Figure 2.* Variation of L_c'/L_s with wave-length. Eyes dark-adapted.

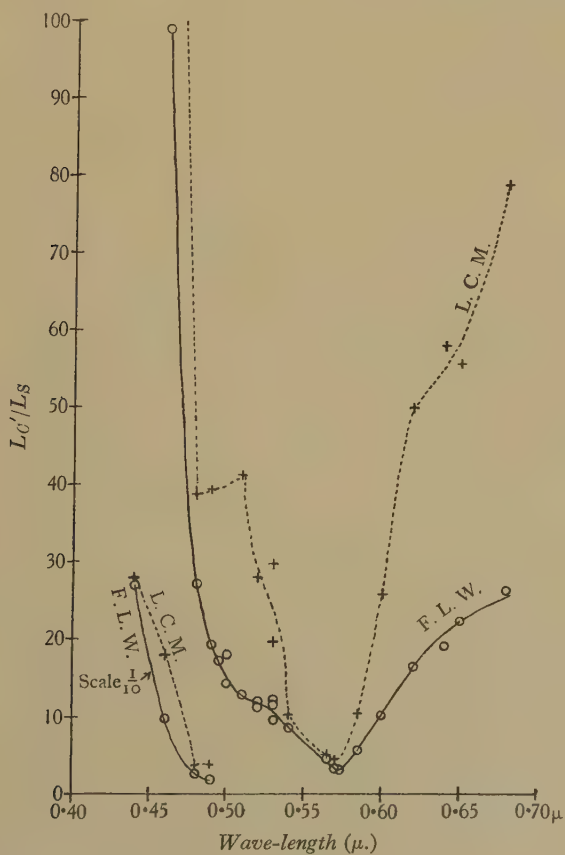


Figure 3. Variation of L_c'/L_s with wave-length. Eyes light-adapted.

* From a paper in the *Discussion on Vision*, pp. 98, 99.

The observations were made with the eye both in the light-adapted state and the so-called dark-adapted state. The most complete set of results obtained by the first method related to the dark-adapted state, and the most complete set obtained by the second method related to the light-adapted state.

§ 2. COMPARISON OF THE RESULTS OBTAINED BY THE TWO METHODS

Both the curves relating the number of steps with λ and L'_C/L_S with λ have been taken as showing the relative saturation of the spectral colours. It is, therefore,

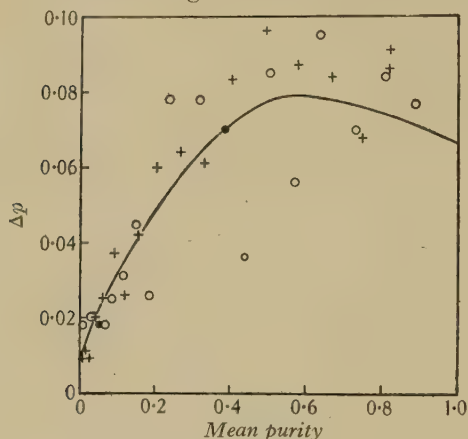


Figure 4. Wave-length, 0.46μ ;
observer, F. L. W.

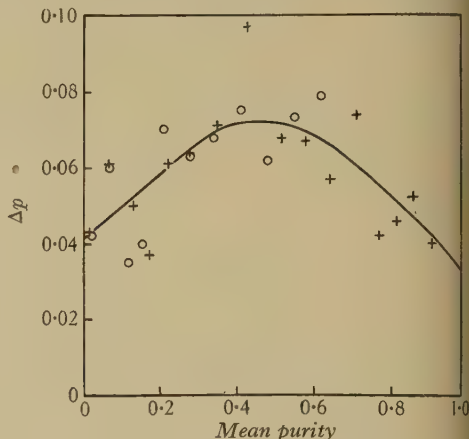


Figure 5. Wave-length, 0.496μ ;
observer, F. L. W.

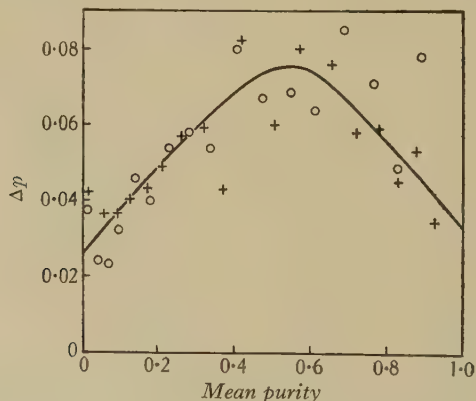


Figure 6. Wave-length, 0.65μ ; observer, F. L. W.

Figures 4-6. Variation in size of limen with purity for different wave-lengths.

important to consider the differences between them. The most striking difference is the saturation for blue as given by L'_C/L_S as compared with that given by the number of steps.

It may be mentioned that if the discrimination limen were the same for all purities for any given hue, the two types of curve would be the same. The reason for the difference must, therefore, be sought in the curves showing the relation between size of limen and purity, figures 4, 5 and 6. These show for blue a great

in the size of the limen with increasing purity, whether the results are obtained by desaturating the spectral colour or by adding blue to white. For the blue colours there is at first a slight increase followed by a decrease to the original

The reason for this difference is obscure; it may possibly be due to eye-movement and lack of foveal fixation, which is very difficult for the blue as has been pointed out by Abney and Watson⁽³⁾. The fact that the rise is more marked for M., who has a very small pigmented area, would favour this view. The total number of steps for the extreme blue cannot, however, be very much in error, and cannot be the same difference between the ordinates for 0.46μ . and 0.50μ . as L_C'/L_S curves, for otherwise the difference in the total number of steps between white and 0.46μ . and between white and 0.50μ ., namely more than 40, would be greater than the total number of steps between these colours on the spectrum itself, namely about 15. If this were so, it would be possible to get fewer steps between white and the extreme blue by first proceeding along the spectrum locus to the green and then desaturating, and this is very unlikely to be the case. These considerations thus point to a greatly decreased sensitivity in the neighbourhood of saturated blue. This view would appear to be supported by some recent work by Munsell⁽⁴⁾ on the sensitivity to difference in hue at different saturations. He found that for hues corresponding to wave-lengths less than 0.49μ . the sensitivity goes through a maximum with decreasing purity instead of continually decreasing. The effect becomes more marked with decreasing wave-length. The effect may be due to extra foveal vision always being used when these colours are viewed.

CORRELATION WITH COMPLEMENTARY COLOUR-MIXTURE DATA

Helmholtz and others have suggested that the ratio of the luminosities in which two colours mix to give white is the inverse of their relative saturations. The most complete set of data on the relative luminosities of such colours when mixed to give white is that due to Sinden⁽⁵⁾. By assuming that the saturation is practically constant in the yellow, he has used his results to give what he calls the relative luminosity of the spectral colours. The resultant curve is very similar to that obtained by plotting L_C'/L_S against λ , and this suggests that the relative luminosities of spectral complementaries is proportional to the relative purities of those colours which are the same hues which are just distinguishable from white. The only direct way of making a precise comparison of the complementary-colour data with the discrimination data is to use the former to obtain the values of L_C'/L_C for the red hues and those for the blue hues, or *vice versa*. This comparison is strictly valid only if the two sets of data refer to the same neutral standard and the same observer. Where such data are available. In the absence of direct data similar to Sinden's (that is, data relating to what has been called the complementation valency), the discrimination can be obtained indirectly from the trichromatic coefficients of the spectral colours and white, provided that the relative luminosities of the unitary colours are also known.

The trichromatic coefficients of the spectral colours and white have been obtained for one observer (F. L. W.) and also the luminosities of the unitary stimuli. The method used for both these sets of observations was identical with

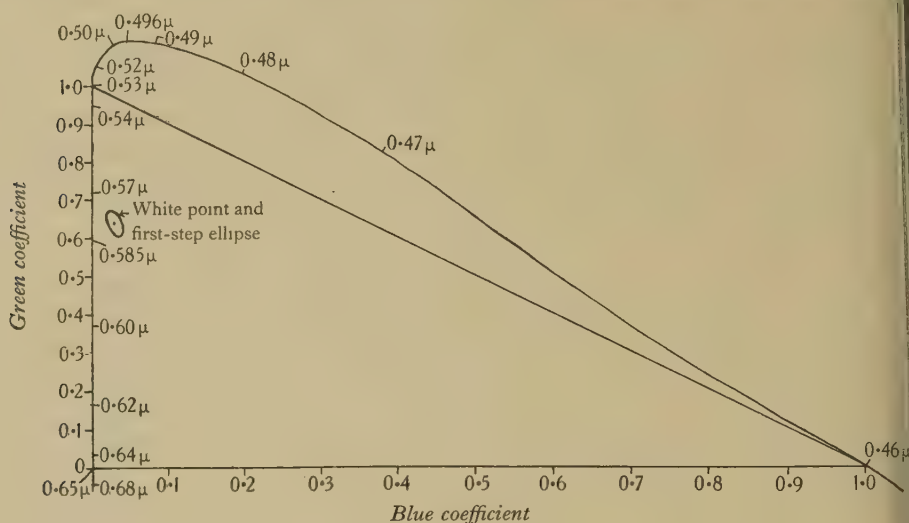


Figure 7 a. Colour triangle showing locus of colours just discriminable from white.

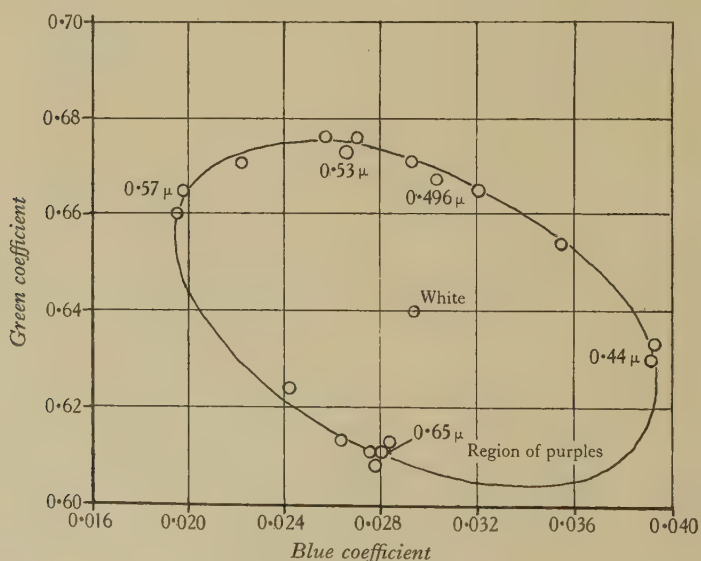


Figure 7 b. Locus of colours just discriminable from white on an enlarged scale.

described by W. D. Wright⁽⁶⁾. For the purpose of determining the luminosity a large number of flicker matches and determinations of the red and blue correction factors were made, a high degree of precision in the results being thus ensured.

By means of the above data, the units in which the unitary stimuli R' , G' and B' are measured can be transformed to the same photometric scale. One trichrom

will then have the same photometric value for all colours. By the use of these coefficients for the spectral colours and white, the coefficients for the colours just discriminable from white can be directly obtained in photometric units, and the locus of these colours in the equal-brightness triangle can be plotted. This is found to be an ellipse with white at the centre.

Alternatively the coefficients so found can be transformed to any other units and the locus is plotted. When this is done the locus remains an ellipse, but the white point is no longer at the centre.

With reference to the equal-brightness triangle, if m is the distance of a spectral colour from white and p the purity of the colour of this hue just discriminable from white, the distance of this latter colour from white is pm . If n and p' are the corre-

m
 p
 n, p'

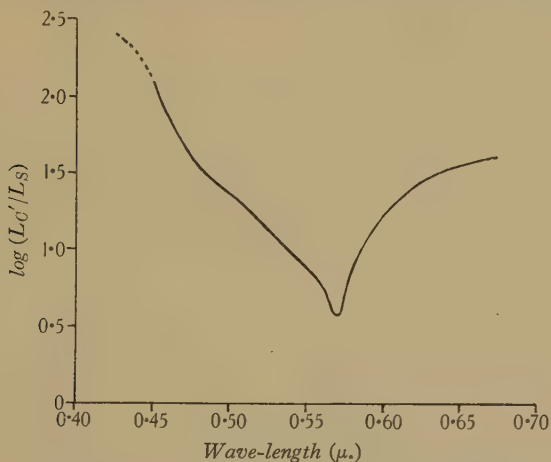


Figure 8. Variation of L_C'/L_S with wave-length; mean logarithmic curve.

ing quantities for the complementary colour, we have—since the colours just discriminable from white lay on an ellipse—

$$\begin{aligned} pm &= p'n, \\ m/n &= p'/p. \end{aligned}$$

m/n is the ratio in which these colours mix to produce white. There is thus a close correspondence between the complementary-colour data and the data concerning colours just discriminable from white.

The curves showing the relation between L_C'/L_S and λ for the observers L. C. M. and L. W. are so similar to those found by Priest and Brickwedde⁽⁷⁾ that after correction of their results by a constant factor, on account of their different field-size, a mean curve has been drawn for all four observers, as being a fairly near approach to the result for a mean eye. These results have been used to obtain a series of points on the locus in the standard triangle of the colours just discriminable from white by a mean observer. The triangle used was that of the C.I.E. Committee on colorimetry with the appropriate luminosity factors. The result is shown in figure 9. The extreme eccentricity of the ellipse is due mainly to the luminosity factors not being representative of the four observers used, but partly

to the fact that the white used by Priest and Brickwedde differs slightly from that of the C.I.E. The distance of many of the points from the curve is due to difficulties in reading the correct value of L'_c/L_s from Priest's curves, especially in the yellow where it is changing rapidly with wave-length.

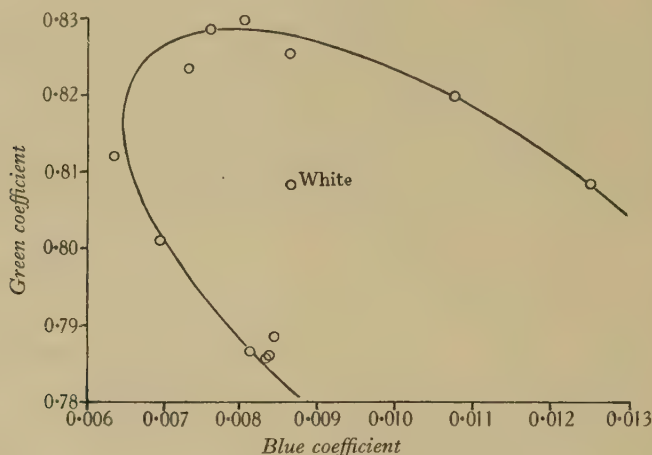


Figure 9. Locus of colours just discriminable from white for a mean observer.

§ 4. INTERPRETATION OF THE RESULTS

Previous attempts to interpret saturation-discrimination by the three-component theory have proceeded along two main lines. The commonest has been the use of the theory to obtain the absolute purity of a colour, together with the postulate that all colours just discriminable from white have the same absolute purity. This has been carried out in the following manner. The general form of the theory states that the trichromatic coefficients of all colours can be transformed to a set of fundamental unitary stimuli R , G and B , for which the coefficients r , g and b are always positive. In this case r , g and b are proportional to the values of the stimuli exerted by the radiation producing the colour upon three independent physiological mechanisms, thus all stimuli which have the same value of r excite the same response in the red receptor.

If we draw a colour triangle using real unitary stimuli R' , G' and B' , these three fundamental stimuli will have co-ordinates $(\rho_1, \gamma_1, \beta_1)$, $(\rho_2, \gamma_2, \beta_2)$ and $(\rho_3, \gamma_3, \beta_3)$. If these points are then joined to form a new triangle, all physiologically possible colours must lie within this triangle, and therefore the colours lying along the boundary are the purest obtainable; they may, therefore, be considered as having unit absolute purity. If the point $(\rho_w, \gamma_w, \beta_w)$ representing white be given zero purity, then since any other colour can be considered to be the result of the mixture of this stimulus and that corresponding to some colour on the boundary, the absolute purity of such a colour will be given by

$$P = L_D/L_C,$$

L_D is the luminosity of the boundary stimulus associated with a quantity of colour having a luminosity L_C .

L_D

the case where photometric units have been used for R' , G' and B' , Newton's colour-mixture gives, figure 10,

$$L_D/L_C = WC/DW.$$

the locus of colours of equal absolute purity is thus a triangle with its sides parallel to those of the triangle RGB and with its apices on the lines WR , WG and BW . It is thus a triangle in any colour triangle. It has, however, been shown above that the locus of colours just discriminable from white is an ellipse. There is thus no connection between absolute purity as defined above and the minimum perceptible

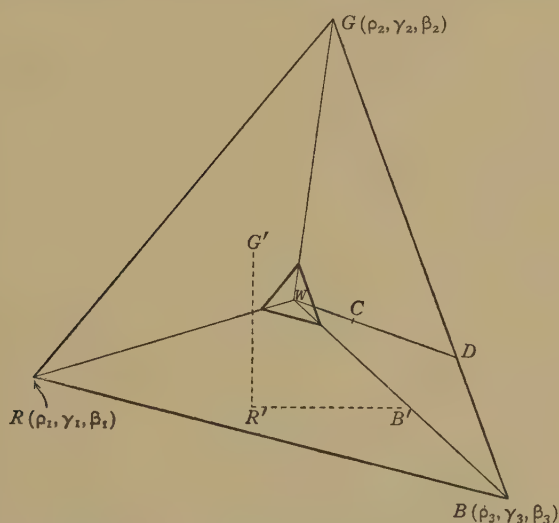


Figure 10. Colours of equal absolute purity.

metric purity, even in the case of complementary colours, which is considered below.

It is frequently assumed that when R , G and B are measured in photometric units the coefficients r_W , g_W and b_W of white are all equal. In this case the absolute purity P_X of a colour X for which r is less than g or b is given by

P_X

$$P_X = \frac{b_X + g_X - 2r_X}{r_X + g_X + b_X} \quad \dots\dots(4.1).$$

A complementary colour Y may then have b less than r or g ,

$$P_Y = \frac{r_Y + g_Y - 2b_Y}{r_Y + g_Y + b_Y} \quad \dots\dots(4.2). \quad P_Y$$

The coefficients are those of unit equations

$$\frac{P_X}{P_Y} = \frac{b_X + g_X - 2r_X}{r_Y + g_Y - 2b_Y} \quad \dots\dots(4.3).$$

On the other hand, if the complementary has g less than r or b ,

$$\frac{P_X}{P_Y} = \frac{b_X + g_X - 2r_X}{r_Y + b_Y - 2g_Y}.$$

If these colours are mixed in the proportion of m units of X and n units of Y they produce white:

$$\begin{aligned} mr_X + nr_Y &= mg_X + ng_Y = mb_X + nb_Y, \\ m(r_X + g_X) + n(r_Y + g_Y) &= 2(mb_X + nb_Y), \\ m(r_X + g_X - 2b_X) &= -n(r_Y + g_Y - 2b_Y), \\ \frac{n}{m} &= -\frac{r_X + g_X - 2b_X}{r_Y + g_Y - 2b_Y} = -\frac{r_X + b_X - 2g_X}{r_Y + b_Y - 2g_Y} = -\frac{g_X + b_X - 2r_X}{g_Y + b_Y - 2r_Y} \dots\dots(4.4). \end{aligned}$$

On such a theory, there is therefore no connection, such as has been assumed by Hecht and other writers⁽⁸⁾, between the absolute purity of complementary colours and the proportions in which they mix to produce white, and therefore there is no connection with the just-discriminable colorimetric purities.

The other method of interpretation of the results on the basis of the three-components theory rests on a suggestion of Helmholtz⁽⁹⁾ that colour-differences arise from intensity-differences among the three independent sensations. Colour-discrimination is, therefore, to be explained by applying Weber's law in some form to the fundamental stimuli R , G and B of the theory. Weber's law states that for colours of moderate brightness the just-perceptible difference of intensity ΔL between two colours is given by

$$\frac{\Delta L}{\bar{L}} = \text{constant} \dots\dots(5.0),$$

where \bar{L} is the mean brightness of the two colours. Applying this to the general case where a colour may change in quality as well as in intensity, we get

$$f\left(\frac{\Delta r}{\bar{r}}, \frac{\Delta g}{\bar{g}}, \frac{\Delta b}{\bar{b}}\right) = \text{constant} \dots\dots(5.1).$$

Since there is to be a perceptible change when there is no intensity-difference, the terms in Δr , Δg and Δb must be of the second order.

The simplest function is

$$\left(\frac{\Delta r}{\bar{r}}\right)^2 + \left(\frac{\Delta g}{\bar{g}}\right)^2 + \left(\frac{\Delta b}{\bar{b}}\right)^2 = \text{constant} \dots\dots(5.11).$$

If the function is to account for brightness-discrimination as well as colour-discrimination, it should include the simple form of Weber's law as a special case. This is, however, not the case with the above simple form, as the value of $\Delta L/\bar{L}$ is different for different colours⁽¹⁰⁾. Schrödinger⁽¹¹⁾ has, therefore, proposed the formula

$$\frac{1}{a_1\bar{r} + a_2\bar{g} + a_3\bar{b}} \left\{ \frac{(\Delta r)^2}{a_1\bar{r}} + \frac{(\Delta g)^2}{a_2\bar{g}} + \frac{(\Delta b)^2}{a_3\bar{b}} \right\} = \text{constant} \dots\dots(5.12),$$

does include Weber's law as a special case. For all changes from a particular

$$x (\Delta r)^2 + y (\Delta g)^2 + z (\Delta b)^2 = \text{constant} \quad \dots\dots(5.2),$$

where units are used for R , G and B .

Various other formulae have been suggested⁽¹²⁾, but they all reduce to the same form when r , g and b are all large compared with Δr , Δg and Δb .

Considering changes in colour alone this equation must be combined with the condition that there is to be no change in brightness. Since the luminosity of colour is given by

$$L_C = L_R r + L_G g + L_B b,$$

the condition is

$$0 = \Delta L_C = L_R \Delta r + L_G \Delta g + L_B \Delta b,$$

$$\therefore \Delta b = -\frac{L_R}{L_B} \Delta r - \frac{L_G}{L_B} \Delta g \quad \dots\dots(5.3).$$

Considering changes in all directions from white, these equations become

$$x (r - r_W)^2 + y (g - g_W)^2 + z (b - b_W)^2 = 0 \quad \dots\dots(5.21),$$

$$(b - b_W) = -\frac{1}{L_B} \{L_R (r - r_W) + L_G (g - g_W)\} \quad \dots\dots(5.31).$$

Considered geometrically, equation (5.21) gives the locus in Lambert's pyramid of colours just discriminable from white, and equation (5.31) is the equation of the equal-brightness plane through white. Their intercept gives the locus in the equal-brightness plane of colours which can just be discriminated from white of the same luminosity, and is an ellipse with white at the centre. When R , G and B are measured in photometric units, this plane is also the unit plane and is the plane of the unit triangle. Hence the locus in the equal-brightness triangle of colours just discriminable from white is an ellipse with white at the centre. In other cases this is not the unit plane; the locus in the unit plane is then the projection from the origin, on to that plane, of the locus in the equal-brightness plane. This also is an ellipse, but the white point will no longer be at the centre since in the projection of a conic from a point not at infinity the centre does not project to the centre.

The theory is thus consistent with the facts of colour-sensitivity in the neighbourhood of white. A satisfactory explanation of the variation in sensitivity with wavelength has not proved to be possible.

§ 5. ACKNOWLEDGMENT

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FINE STRUCTURE IN THE (2D) SERIES LIMIT TERMS OF THE I^+ SPECTRUM

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Communicated by Prof. W. L. Bragg, F.R.S., July 16, 1935.

Read in title October 18, 1935

TRACT. The eleven lines of the I^+ spectrum which were previously analysed for structure belong to the (4S) system. The analysis is now extended to the (2D) system, seven lines having been analysed and fine-structure interval factors found for twelve. This brings the known number of interval factors up to twenty-three. Large interval factors are found associated with the $5d$ electron terms of both the systems. This is related with observations in the Sn II fine structures, and it is shown that the large interval factors are due to perturbation by terms with large fine structure. Two types of perturbation in the fine structures are observed.

§ 1. INTRODUCTION

THE author has already published measurements of the fine structures of the visible lines in the first spark spectrum of iodine⁽¹⁾. At the time of writing only a partial analysis of the gross multiplet structure was available, Murakawa⁽²⁾ being responsible for this classification. Eleven out of the forty-two lines whose fine structures were recorded, were classified by Murakawa. From these lines it was proved that the nuclear spin of iodine is $5/2$, this value being later confirmed by an analysis of the fine structures in the arc spectrum of iodine⁽³⁾. Recently a very thorough multiplet classification for I^+ has been made by Lacroute⁽⁴⁾, who by employing the Zeeman effect classified over two hundred lines and identified fifty-four terms. The Zeeman-effect observations agree with the $5/2$ value for the nuclear spin. Lacroute showed that the analysis given by Murakawa was correct, and further that all the lines classified by Murakawa and analysed for fine structure⁽²⁾ are lines in which both the terms go to the (4S) series limit. Amongst the forty-two previously recorded fine structures, fourteen lines have both terms going to the (2D) series limit, according to Lacroute. No intercombinations between the (4S) and (2D) terms occur in the group of lines observed, so that a complete analysis is required in order to determine the fine structures in the (2D) series terms. The object of this paper is to give an account of the fine-structure analysis of twelve of these terms. The line transitions studied are shown in figure 1, in which it is seen that most of the terms are involved more than once. The concordance between the values of the fine-structure interval factors when calculated from more than one line serves therefore as an indication of the reliability of the values found.

In the (4S) terms all the lines examined except one are transitions between $5p^3ns$ and $5p^36p$. The largest interval factor for a $5p^36p$ term is $25 \text{ cm}^{-1} \times 10^{-3}$, whilst the two important s terms 6^5S_2 and 7^3S_2 have interval factors of 100 and 26 respectively. Hence a number of the structures are easy to analyse because the

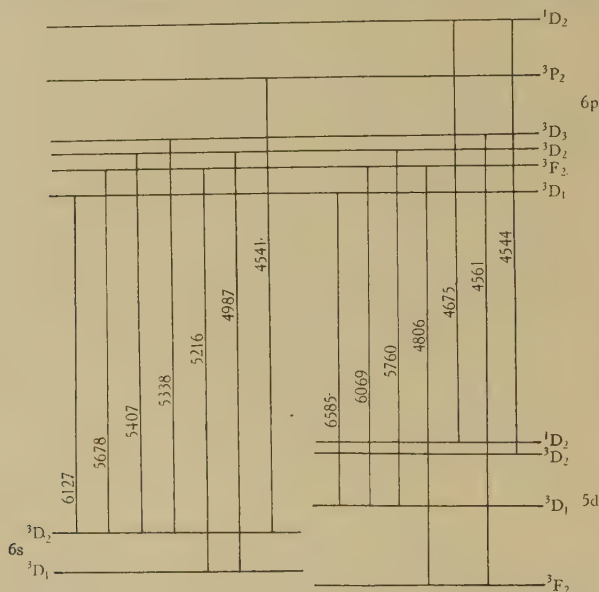


Figure 1. Line transitions involving (2D) series limit terms.

upper and lower interval factors have a large ratio. The (2D) terms are somewhat different; most of the structures are irregular and imperfectly resolved. This is due both to the approximate equality of the upper and lower interval factors in many cases, and to the fact that many of the lines lie in the blue, where the instrumental resolution has fallen off.

§ 2. OBSERVATIONS

The measurements are taken from the author's previous publication⁽¹⁾. Since new allocations are known, the structures of the lines which have been classified and also analysed are shown in table 1. The lines indicated by an asterisk are those analysed here, and in these both the terms go to the (2D) limit. The other lines involve the (4S) limit and have already been analysed, but are included to complete the table.

§ 3. ANALYSIS

It is apparent from most of the structures that the interval factors in both the terms of a line are of the same order, a fact which makes analysis difficult and in some cases ambiguous. As the nuclear spin is $5/2$, each line has a large number of components, e.g. a frequently occurring transition for which $\Delta J = 2 \rightarrow 2$ has thirteen components, so that if the two interval factors are similar the blending can become

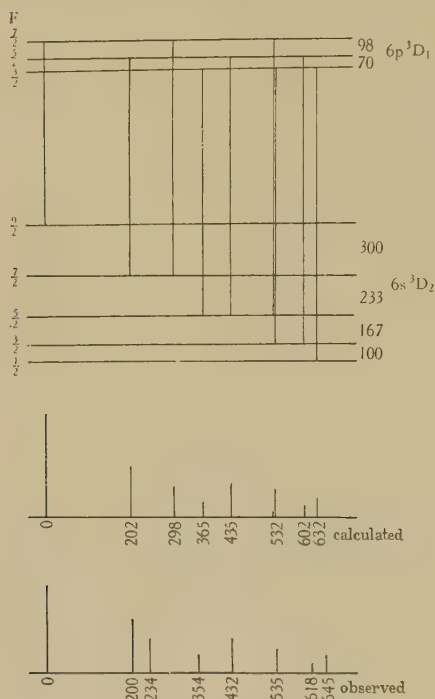
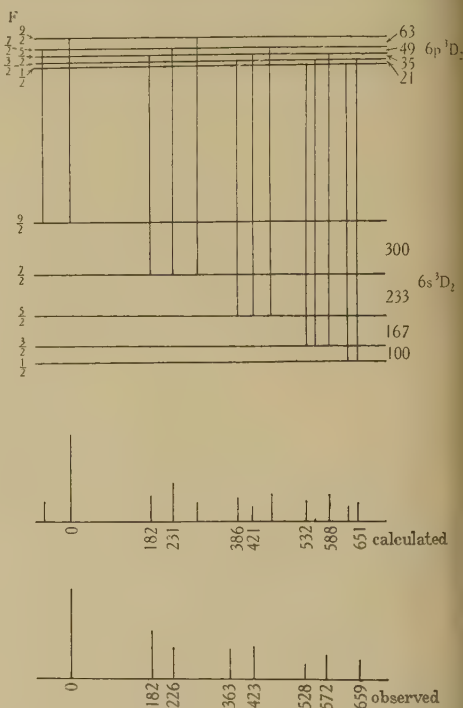
Table 1. Fine structures in the classified lines of the I⁺ spectrum .

Wave-length	Classification	Structure (cm. ⁻¹ × 10 ⁻³) violet									
5585.0*	5d ³ D ₁ -6p ³ D ₁	0 (2)	47 (6)	178 (3)	256 (2)						
56127.4*	6s ³ D ₂ -6p ³ D ₁	0 (10)	200 (6)	234 (4)	354 (2)	432 (4)	535 (3)	618 (1)	645 (2)		
56068.8*	5d ³ D ₁ -6p ³ F ₂	0 (2)	35 (3)	126 (10)	251 (4)	308 (15)					
55950.1	6s ³ S ₁ -6p ³ P ₁	0 (3)	47 (3)	121 (2)	204 (4)						
55920.7	6p ³ P ₀ -7s ³ S ₁	Single									
55787.1	6p ³ P ₂ -7s ³ S ₁	0 (4)	56 (1)	106 (2)	149 (2)						
55774.7	5d ³ D ₂ -6p ⁵ P ₁	0 (5)	741 (4)	1291 (3)	1686 (2)	1913 (1)					
55760.4*	5d ³ D ₁ -6p ³ D ₂	0 (10)	56 (3)	100 (5)	132 (4)	159 (4)					
55678.0*	6s ³ D ₂ -6p ³ F ₂	0 (1)	86 (3)	173 (10)	238 (4)	293 (3)	424 (3)	482 (6)			
55625.7	6s ³ S ₁ -6p ³ P ₂	0 (2)	28 (2)	70 (3)							
55504.8	6s ³ S ₁ -6p ³ P ₀	0 (1)	33 (1)								
55496.8	6s ⁵ S ₂ -6p ⁵ P ₁	0 (5)	429 (4)	756 (3)	991 (2)	1141 (1)					
55464.8	6s ⁵ S ₂ -6p ⁵ P ₂	0 (10)	303 (1)	363 (4)	415 (2)	630 (3)	680 (3)	840 (2)	868 (3)	969 (3)	
55407.3*	6s ³ D ₂ -6p ³ D ₂	0 (16)	182 (8)	226 (7)	363 (6)	423 (6)	528 (2)	572 (4)	659 (4)		
55338.2*	6s ³ D ₂ -6p ³ D ₃	0 (1)	107 (8)	236 (6)	348 (4)	429 (2)	461 (1)				
55216.2*	6s ³ D ₁ -6p ³ F ₂	0 (3)	22 (1)	79 (3)	122 (4)	199 (5)	283 (6)	366 (12)			
55161.2	6s ⁵ S ₂ -6p ⁵ P ₃	0 (5)	397 (4)	695 (3)	905 (2)	1025 (1)					
55156.4	6p ⁵ P ₁ -7s ⁵ S ₂	0 (2)	75 (3)	163 (4)	266 (5)	382 (6)					
55087.0*	6s ³ D ₁ -6p ³ D ₂	0 (4)	38 (3)								
5506.4*	5d ³ F ₂ -6p ³ F ₂	0 (4)	53 (5)	121 (5)	168 (6)	213 (6)	252 (12)	293 (2)			
55675.5*	5d ¹ D ₂ -6p ¹ D ₂	0 (12)	150 (4)	295 (10)	365 (20)	508 (4)	673 (3)				
55632.4	6s ⁵ S ₂ -6p ³ P ₂	0 (5)	399 (4)	695 (3)	928 (2)	1054 (1)					
55610.0*	5d ³ F ₂ -6p ³ D ₃	0 (1)	-----		228 (4)						
55544.3*	5d ³ D ₂ -6p ¹ D ₂	0 (3)	240 (2)	373 (5)	685 (1)						
55540.9*	6s ³ D ₂ -6p ³ P ₂	0 (2)	110 (1)	162 (1)							
55488.8*	5d ³ D ₁ -6p ³ D ₁	0 (2)	117 (1)	162 (1)							

† Previously given as 5679.0 by mistake.

so serious that the interpretation is difficult. There are two lines in which the resolution is good and in which the upper interval factors are reasonably small compared with the lower term, namely $\lambda 6127.4$ and $\lambda 5407.3$. $\lambda 6127.4$ is $6s^3D_2 - 6p^3D_1$ and as the upper term has $J=1$ the line shows a simpler structure than $\lambda 5407.3$, for which $\Delta J = 2 \rightarrow 2$.

The analysis of this line, which has been carried out with a reasonable degree of precision, is shown in figure 2. The lower interval factor is 66.6, and although the upper is 28 the small value of J for the upper term produces a simplification in the pattern. Figure 3 shows the analysis of $\lambda 5407.3$ and the agreement between the

Figure 2. $\lambda 6127.4$.Figure 3. $\lambda 5407.3$.

calculated and observed patterns is reasonably good. In both cases the discrepancies are probably due to the difficulty of measurement.

It is important to notice that these analyses, which, as in the case of the (45) lines, have been carried out by the Fisher-Goudsmit method⁽⁵⁾, presuppose the validity of the interval rule. It has been shown in the previous work on the fine structures in the arc and spark spectra of iodine that perturbations occur in some terms, and this fact must be considered in dealing with the present case. If a term is perturbed with a breakdown in the interval rule it is still possible to obtain an approximately correct value for the interval factor, but in the Fisher-Goudsmit diagram some components will be out of place.

Owing to the incompleteness of the resolution of the structures and also to the probable occurrence of deviations from the interval rule occasioned by perturbation,

interval factors found for a given term vary somewhat when calculated from different lines. In quite a number of the lines analysed a component was found to be displaced. The following examples show the degree of variation in the calculated interval factors. Both $\lambda\ 6127\cdot4$ and $\lambda\ 5407\cdot3$ give 66.6 as the interval factor, hence denoted by A , for $6s\ ^3D_2$ and approximately the same value is found from $\lambda\ 5678\cdot0$, $5338\cdot2$, $4540\cdot9$ which also involve this term. For the term $6p\ ^3F_2$ the three lines $\lambda\ 5678\cdot0$, $5216\cdot2$, $4806\cdot4$ give A as ~ 47 , 40 , 36 respectively. Thus 40 may be taken as an approximate value, the error being about 10 per cent. The values for $6p\ ^3D_2$ given by $\lambda\ 5407\cdot3$ and $\lambda\ 4987\cdot0$ are both equal to 14 . The line $\lambda\ 5338\cdot2$ gives $A=\sim 27$ and $\lambda\ 4561\cdot0$ gives $A=\sim 22$ for the term $6p\ ^3D_3$. The former value

A

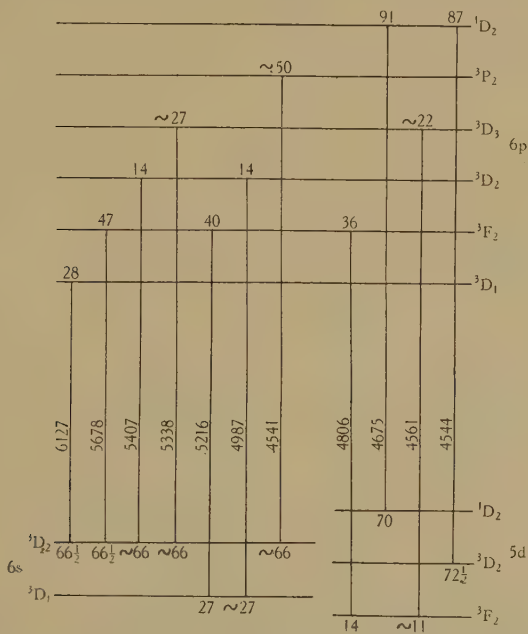


Figure 4. Interval factors calculated for each line transition.

considered the more reliable, so that A is taken as ~ 25 for this term. One more example will be quoted and that is the upper term $6p\ ^1D_2$, which has the largest interval factor observed for the (²D) terms. $\lambda\ 4675\cdot5$ and $\lambda\ 4544\cdot3$ both exhibit extremely wide structures, and although the region is not one which gives very good resolution with a silvered Fabry-Perot interferometer, the values found for A for the term in question are 91 and 87 respectively. The mean value, 89, is probably close to the true value. The three lines $\lambda\ 6585\cdot0$, $6068\cdot8$, $5760\cdot4$ are of interest, for it was found impossible to fit these into Fisher-Goudsmit patterns. All involve $5d\ ^3D_1$ as the lower term. This lower term must therefore be very strongly perturbed. An approximate estimate for A shows that it probably lies between 25 and 40. It should be mentioned that a very faint component which had only been detected in $\lambda\ 5216\cdot2$ is probably non-existent, the analysis showing that it is

superfluous. It had been previously recorded as a line of strength 1, only 75 units away from a line of strength 24.

Figure 4 shows the line transitions which have been analysed, and at the ends of each line the interval factors calculated for that line are indicated. Line transitions are only schematic and not to scale.

§ 4. DISCUSSION OF RESULTS

All the interval factors now known for the I^+ spectrum are collected together in table 2. The degree of accuracy is much higher in the (^4S) terms than in the (^2D) terms, the error varying from 1 to 5 per cent in the former whilst in the latter the interval factors are only known to within 10 per cent except in the three largest values, which are fairly accurate. In the terms marked with a sign of approximation the error may exceed 10 per cent.

Table 2. Interval factors in the I^+ spectrum ($\text{cm}^{-1} \times 10^{-3}$)

(^4S)		(^2D)	
$6s\ ^5S_2$	100	$6s\ ^3D_1$	27
$7s\ ^5S_2$	26	$6s\ ^3D_2$	$66\frac{1}{2}$
$6s\ ^3S_1$	$5\frac{1}{2}$		
$7s\ ^3S_1$	Small		
$6p\ ^5P_1$	10	$6p\ ^3P_2$	~ 50
$6p\ ^5P_2$	~ 20	$6p\ ^1D_2$	89
$6p\ ^5P_3$	10	$6p\ ^3D_1$	28
$6p\ ^3P_0$	0	$6p\ ^3D_2$	14
$6p\ ^3P_1$	~ 25	$6p\ ^3D_3$	~ 25
$6p\ ^3P_2$	11	$6p\ ^3F_2$	40
$5d\ ^3D_2$	166	$5d\ ^1D_2$	~ 70
		$5d\ ^3D_1$	(?) 25-40
		$5d\ ^3D_2$	72
		$5d\ ^3F_2$	14

An important point revealed by the table is that many of the $6p$ and $5d$ electron terms have very large interval factors relative to those of the $6s$ electron terms. According to the usual assumptions it is not to be expected that the $6p$ and $5d$ electrons should be equal in penetrating power to the $6s$ electron, hence the implication is that the $5p^3$ group contributes to the value of the interval factor to an appreciable degree. A similar effect was observed in the p^4 groups of the iodine and bromine arc spectra.

The difference between the $6p$ terms belonging to the (^4S) and (^2D) systems is due to the rearrangement of the $5p^3$ group, and as there is a marked difference in the interval factors of the two sets of $6p$ terms it is apparent that the $5p^3$ group makes an important contribution. The electron coupling is partially jj , as is shown by the irregularity of the multiplets, so that $5p_{\frac{1}{2}}$ electrons will exist, and as a $p_{\frac{1}{2}}$ electron may behave in a heavy atom as if it were partially penetrating, moderately large nuclear coupling can exist for the $5p^3$ group. Thus the experimental values for the $6p$ terms fit in with expectation.

The most outstanding fact shown by the table is that most of the $5d$ electron terms have large interval factors, in fact the largest yet observed belongs to this group. It is very unlikely that a $5d$ electron can exhibit even partial penetration. If pure jj coupling is assumed there will then exist $d_{3/2}$ and $d_{5/2}$ electrons, and most the $d_{3/2}$ electron will be comparable in penetrating power with a $p_{3/2}$ electron, so that the coupling will be very small. The large interval factors can be explained, however, as a perturbation effect. There are two types of perturbation. In the first, observed by Shenstone and Russell⁽⁶⁾, two terms which are produced by different electron configurations, have the same L , S , J , and are both odd or both even, can disturb each other even if they are many thousands of cm^{-1} apart. In a perturbation of this type the wave functions characteristic of both the electrons mix, so that one of the perturbing terms has a very wide fine structure associated with it the other term partakes of this property and also acquires a wide fine structure, the width depending upon the degree of perturbation. The interval rule holds accurately in such perturbed fine structures, only the value of the interval factor being determined by the perturbation. The second type of perturbation, which was found by Schüller and Jones⁽⁷⁾ in Hg I and also occurs in the iodine arc spectrum, is due to an accidental close approach of two terms. In this type the fine-structure interval is broken in at least one of the terms if the values of J differ.

The (2D) $5d^3D_1$ perturbation is doubtless of the second kind, for the interval rule appears to be broken. On the other hand the large values of the other $5d$ terms are due probably to perturbations of the first kind. Consider first (4S) $5d^3D_2$ with an interval factor 166. The table shows that this large interval factor is not due to the $5p^3$ group, for $6s^5S_2$, in which the $6s$ electron is of most importance, has an interval factor of only 100. As the factors for $7s^5S_2$ and $6s^5S_2$ are 26 and 100 respectively, it is reasonable to expect that a $5s$ electron would produce an interval factor of at least 400 and even possibly much more. The normal state of I^+ is $5s^2 5p^4$, the $5d^3D_2$ term being produced by a displacement of a $5p$ electron to a $5d$ orbit. However the $5s^2$ shell can be broken, giving $5s5p^5$, $5s5p^46s$, $5s5p^46p$, etc., the term containing an unpaired $5s$ electron so that there are very large interval factors in many of the terms. Moreover as the coupling is neither LS nor jj the perturbation selection rule as to L and S will not be rigidly obeyed, for strictly speaking these vectors have no real meaning in such a case. It is very probable that one of these terms perturbs (4S) $5d^3D_2$, and because the interval factor of the perturbing term is so large a value of 166 can easily result for (4S) $5d^3D_2$ even if the terms are of the order of say $40,000 \text{ cm}^{-1}$ apart, which is the order of the energy required to break up $5s^2$.

It may be noted that the interval rule is still accurately obeyed after perturbation, and the measurements show this to be so. An analogous case of an increase in interval factor associated with a $5d$ electron was found by the author⁽⁸⁾ in the fine structures. Here the $5s^2 5d^2D_{5/2}$ term has an interval factor 130 whilst that of $5s^2 6s^2S_{1/2}$ is 207. The perturbation effect is no doubt similar.

The large interval factors in the (2D) $5d$ electron terms are probably due in part to perturbation and in part to the contribution of the $5p^3$ group which appears to

have a larger coupling constant when going to the (2D) limit than when going to the (4S) limit. However there seems to be strong evidence of perturbation. The large interval factor for (2D) $6p\ ^1D_2$ implies a perturbing mechanism similar to that producing the large interval factor in (4S) $5d\ ^3D_2$. The same is perhaps true for (2D) $5d\ ^1D_2$ and (2D) $5d\ ^3D_2$.

§ 5. ACKNOWLEDGMENTS

I wish to express my thanks to Dr R. Peierls for helpful discussion on the question of perturbations. I wish also to take this opportunity of thanking Prof. W. L. Bragg, F.R.S., for the admirable experimental facilities granted me whilst I was carrying out this work.

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ABSOLUTE INTENSITIES IN THE SPECTRUM OF LOW-PRESSURE QUARTZ MERCURY-VAPOUR DISCHARGE BURNER

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ABSTRACT. Absolute intensities of the main wave-lengths between 6000 and 2400 Å. obtained by a commercial type of a very low-pressure mercury-vapour discharge burner are calculated, and some theoretical aspects of the results as compared with those for high-pressure arcs are considered. Therapeutic effects of the two types of burner are discussed in reference to the production of erythema.

§ 1. INTRODUCTION

In a recent paper⁽¹⁾ values for the absolute intensities of the main wave-lengths of the mercury arc spectrum were given for high-pressure arcs, i.e. arcs where the vapour pressure of the mercury is of the order of 1 atmosphere. Various types of mercury-vapour burner are made; they operate at pressures ranging between this high value and a fraction of a millimetre, i.e. with the tube barely warm. The latter type, which is often referred to as the "cold quartz" type, are used therapeutically as they may be placed in contact with the skin without fear of temperature burns.

In the present below data obtained on such a low-pressure type of burner, the vapour pressure being of the order of 0.01 mm. The discharge in tubes of this type is made between cold metallic electrodes, the tubes operating with a moderately high voltage a.c. supply. For this particular type about 600 volts is required to start the discharge and about 300 volts to maintain it, sufficient leakage reactance being provided in the step-up transformer to stabilize the current. The tube passes about 2 A., so that the power in the discharge is only 45 watts in this case.

§ 2. PROCEDURE

Direct measurements with a spectroradiometer are not possible for these very low-pressure sources, as the intensities of all lines, except the resonance line, are very weak. The results given herewith were obtained by a spectrophotometric method whereby two magnesium-oxide screens were illuminated, one by the test source placed 100 cm. (the standard distance for which intensities are quoted) away, and the other by a standard high-pressure arc whose intensities for all the main wave-lengths had been carefully determined by the spectrometric method described in the previous paper⁽¹⁾. The intensity of radiation on the magnesium-

oxide screen was varied in known manner by moving this standard source to various distances along the optical bench and deducing the actual intensity at the screen by means of the inverse-square law and the calibration values for one fixed distance. Radiation falling on the two magnesium-oxide screens then entered a spectrograph with a Hufner rhomb before the collimator slit, and in this way juxtaposed spectra were obtained on the photographic plate. From these spectra records of equal photographic density were obtained and hence the intensities of the test source were deduced from the known values for the standard.

§ 3. RESULTS AND DISCUSSION

The results obtained are given in table 1. As is to be expected, the resonance line 2536.5 Å. is very intense since the mercury-vapour pressure is so low that absorption in the outer layers of the vapour and self-reversal are practically absent. It will be noted that this line is 98 times as intense as the line at 4358 Å. and accounts for 90 per cent of the total output of all the lines measured. Thus the intensity in the visible region of the spectrum is no guide to that in the short-wave ultra-violet.

Table 1. Radiant energy flux ($\mu\text{W./cm}^2$) at 1 metre from the centre of quartz mercury-vapour burners

Wave-length (Å.)	A.-c. discharge type. 300 V. 150 mA., very low pressure	A.-c. high-pressure arc type. 3.6 A. to common cathode
5780	0.17	38.2
5461	1.05	41.6
4358	1.20	35.3
4047	0.47	20.2
3650	0.65	56.0
3342	0.04	6.1
3132	0.71	40.3
3022	0.07	16.0
2967	0.22	9.1
2894	0.05	4.6
2804	0.02	6.5
2753	0.03	—
2652	0.07	16.1
2536	120.0	19.9
2482	0.03	5.1
Total	125	314
Total for λ 3132 and shorter wave-lengths	121	117

We have not determined the intensity of so many lines as in the high-pressure arcs; we obtained values for only the first two members of the sharp series and the first three of the diffuse series. However, when the logarithm of the intensity is plotted as before against wave-number, figure 1, the members of the diffuse series show a linear relation in contrast to the curves given in figure 4 of the previous paper⁽¹⁾ for the high-pressure arc. Hence Hulburt's⁽²⁾ theoretical relation is fol-

and closely, at least by these few lines, in the low-pressure mercury discharge. This indicates that his probability function α is constant for the lines of a series under these conditions. The general agreement in the slopes of the sharp series, and the greater slopes of the several diffuse series found in the high-pressure arcs, are maintained in this low-pressure discharge, and from these slopes we deduce

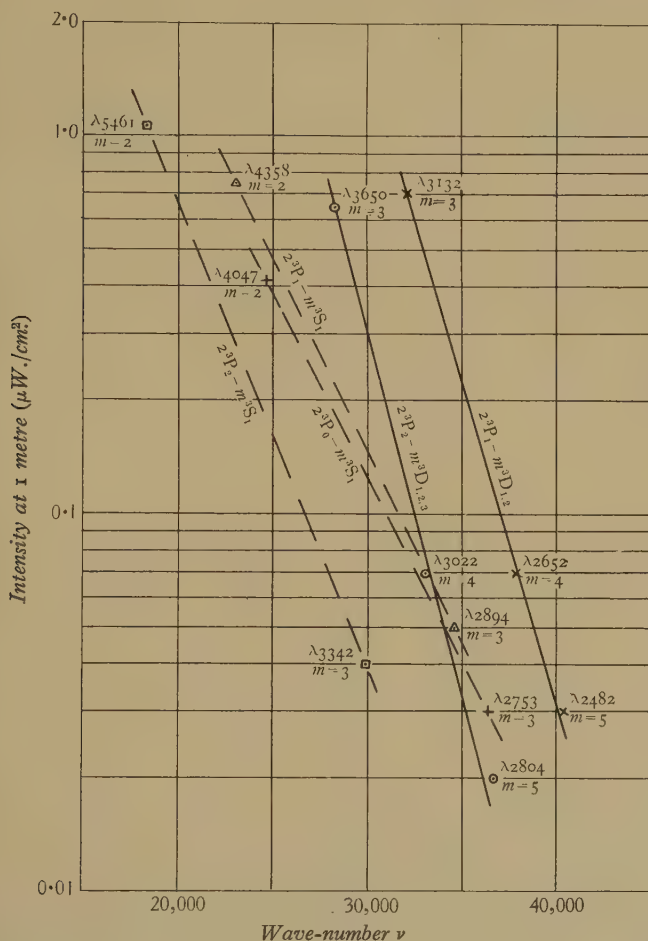


Fig. 1. Relation between intensity and wave-number for the sharp and diffuse series of the mercury spectrum in low-pressure discharge.

approximate values of $5900^\circ K.$ and $3500^\circ K.$ for the temperatures of the excited arcs in the 2^3S and 2^3D levels respectively. McAlister's⁽³⁾ relations for his low-pressure arc show a tendency towards a more linear relation. On the basis of the current and voltage ratings of his burners the vapour pressure in McAlister's determinations would be intermediate between the pressure in the high-pressure arcs of the previous paper⁽¹⁾ and the low pressure of the discharge burner used in the present investigation. It appears, then, that with increase of vapour pressure,

departure from the theoretical relation becomes more marked, especially for lines in the diffuse series.

From a comparison of figure 1 and figure 4 of the previous paper⁽¹⁾ it will be seen that, as the vapour pressure of the mercury changes from a low to a high value, the relative intensity-distribution throughout the spectrum changes. Thus, whereas at low pressure the $2^3P_2 - m^3D_{1,2,3}$ series ($\lambda\lambda$ 3650, 3022, 2804, ...) is relatively weaker than series having as their first members λ 3132, λ 4358 and λ 5461, at high pressure the intensities of all the lines in this series have increased until it is relatively the strongest. Similarly the $2^3P_1 - m^3D_{1,2}$ series increases relatively in intensity until, at high pressure, the first member, λ 3132, is comparable in intensity with λ 5461, the first member of $2^3P_2 - m^3S_1$, whereas at low pressure it was only 68 per cent as intense.

It will be noted that this source, which appears to emit weakly as judged by the visible output, is actually quite a powerful source of ultra-violet radiation of wave-length 2536.5 Å. The absolute intensity of that wave-length in this burner, which consumes only 45 watts in the arc, is greater than the total intensity of $\lambda\lambda$ 2536.5 and 2534.8 together in the high-pressure 3.5-Å. burner no. 160, which consumes 495 watts in the arc; it is in fact nearly 1.6 times as intense.

§ 4. THERAPEUTIC EFFECTS

It is of interest to see how the high and very low-pressure mercury burners compare as regards therapeutic effects, since their intensity-distribution is so different, the high-pressure type having a spectrum with numerous strong lines of more or less comparable intensity, and the very low-pressure type emitting practically the whole of its output in one very intense line at 2536 Å. We shall consider only the production of erythema, since this is often taken as a guide for treatment in many clinical cases, and in the cure of rickets has been found to be a close guide to the results obtainable.

Only wave-lengths below 3200 Å. produce erythema, and even these vary greatly in their effect, the maximum being produced at a wave-length of 2967 Å. Although individuals vary considerably in the energy necessary to produce reddening of the skin, determinations of the relative effects of the various wave-lengths by several individual workers all agree reasonably well, the greatest divergence occurring at the shorter wave-lengths. Such determinations have been made by Hausser⁽⁴⁾, by Luckiesh, Holladay and Taylor⁽⁵⁾ and by Coblenz, Stair and Hogue⁽⁶⁾, and the mean of the results obtained by these various experimenters are given in figure 2, which shows the relative erythema effectiveness referred to unit effect at λ 2967 Å. In other words, the curve shows the effectiveness which each wave-length would have in producing a minimum perceptible erythema if it were of the same intensity as λ 2967. Hence from this curve we can obtain the equivalent intensity of λ 2967 for any source if we have determined the intensities of the various spectral lines in absolute value by multiplying these values by the corresponding erythema effectiveness and summing the results. The sources are then directly comparable in respect

ly of their absolute intensity but also of their effectiveness in producing
ma.*
e wave-lengths 3132, 3022, 2967, 2894, 2804, 2652, 2536, 2482 Å., of which
2652 and 2536 are understood to include groups, are those most responsible
mercury spectrum for production of erythema. For these wave-lengths we
total power of $268\mu\text{W./cm}^2$ at 100 cm. from the high-pressure 2.5-A. burner
4, whilst the low-pressure burner gives $121\mu\text{W./cm}^2$ at the same distance.
atter burner has thus 0.45 times the total intensity of the former. However,
process described above, it is found to be 0.6 times as effective as regards the
ction of erythema, owing almost exclusively to the intense line at 2536 Å.

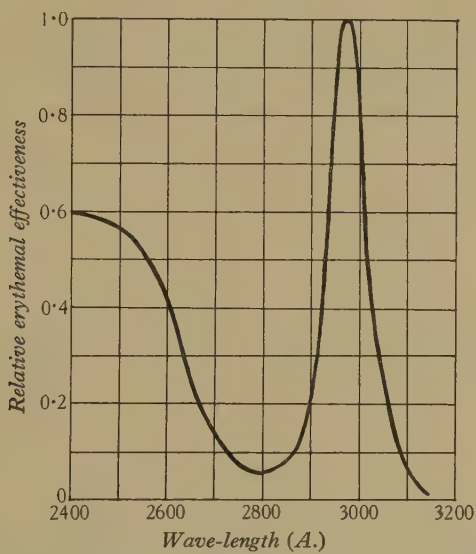


Figure 2. Relative effectiveness of various wave-lengths in producing erythema.

n, in a therapeutic aspect, this low-pressure discharge burner can be con-
as a source of monochromatic radiation of wave-length 2536 Å.
a obtained with an a.-c. high-pressure type of mercury-vapour burner with
odes and a common mercury-pool cathode are also given in table 1 for com-
3. It will be noted that the total intensity of wave-lengths below 3200 Å. for
arner and for one of the low-pressure discharge type are comparable, the
on from the discharge burner being 1.1 times as intense for these wave-
though only 0.4 times as intense if all wave-lengths are considered. How-
n the basis of effectiveness in producing erythema, calculation of the product
lute intensity-values and the relative values given in figure 2 shows that the
pressure burner would be 1.4 times as effective.
Experimental confirmation of this conclusion was obtained by exposing the
copper (untanned) arm first to the low-pressure burner and then, adjacently,
erythema, in the sense in which we use it in this discussion, is taken to be the minimum
ole erythema, often referred to as "M.P.E."

to the high-pressure burner for a graded series of exposure-times and at a distance of 100 cm. in each case. Minimum perceptible erythema was produced in 3 minutes by the low- and in 4 minutes by the high-pressure burner, showing the former to be 1.3 times as effective in producing erythema. This result is in sufficiently good agreement with the calculated value of 1.4. Direct comparison made, as above, on the same person on neighbouring areas of skin and at about the same time are reliable.

Data on the total energy of λ 2967 or its equivalent required to produce minimum perceptible erythema is meagre, and the results obtained by two groups of experimenters show a wide divergence although amongst the three individuals of each group the results were in fair agreement. Thus Luckiesh, Holladay and Taylor⁽⁵⁾ give $4300 \mu\text{W} \cdot \text{sec.}/\text{cm}^2$ as the mean of a number of determinations made on these three workers, whilst Coblentz, Stair and Hogue⁽⁷⁾ give $20,500 \mu\text{W} \cdot \text{sec.}/\text{cm}^2$ as their mean value. However, different parts of the body and different persons react differently to ultraviolet radiation, and it is not surprising that marked differences are obtained in any experimental determinations of this nature. It is probable that these two sets of data can be taken, more or less, as limits between which the energy required to produce the minimum perceptible erythema on any one person might lie.

The exposures made by the author of 3 minutes and 4 minutes for the low- and high-pressure burners under consideration correspond to about $11,500 \mu\text{W} \cdot \text{sec.}/\text{cm}^2$ of radiation of wave-length 2967 Å., or about the mean of the two sets of data referred to above.

§ 5. ACKNOWLEDGMENTS

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EXPERIMENTS ON CONDUCTING LAMINAE IN PERIODIC MAGNETIC FIELDS

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ABSTRACT. The secondary magnetic field due to conducting circular discs, placed in a spatially uniform magnetic field which alternates with time, has been measured and it has been found that as the dimensions of the disc, the conductivity, and the frequency increase, the secondary field also increases and the phase-difference between the secondary field and the primary field changes from $\pi/2$ to 0. Simple considerations show that these results appear for all conductors or conducting laminae of similar shape, no matter how they are excited. The results have been applied to the practical case of the location of good conducting mineral lodes beneath the earth's surface.

§ 1. INTRODUCTION

ONE method of geophysical prospecting⁽¹⁾ consists in inducing currents in good conducting bodies, such as metal sulphides, by the application of an alternating magnetic field, the presence of the conductor being detected by the secondary magnetic field set up by the currents induced. Although small-scale experiments on this method have been carried out by several observers, either they have been conducted with types of bodies which do not approximate in shape to those occurring in the field, or sufficient detail has not been given in the published results. Thus Slichter⁽²⁾ has performed experiments on conducting spherical shells and in the field due to a loop and has compared his results with those calculated for such a body placed in a uniform field. Sundberg⁽³⁾, on the other hand, has determined the field due to rectangular sheets excited by an alternating current flowing in a rectangular loop, thus reproducing approximately the conditions occurring in practice. Full details of the latter experiments are not given and it is not possible to determine from them the factors which control the secondary field due to a body.

In the following experiments were made with the object of determining the above factors. Various circular discs, placed with their planes perpendicular to a spatially uniform magnetic field alternating with time, were used to represent the conducting body in the applied magnetic field. To some extent this is open to the objection that it applies to Slichter's results, but since mineral deposits approximate closely to sheets rather than to spheres or spherical shells, the results throw light on the magnitude of the distortion of the magnetic field due to such bodies and on the factors upon which the response depends, particularly the thickness, resistivity and frequency. To some extent, by using discs of different radii, the effect of the linear dimensions of the sheet has been investigated.

The uniformity of the applied magnetic field was essential to ensure that the discs, no matter what their dimensions, should be excited in the same way, while the circular shape of the metal plates was chosen because, by using the fact that the field is the same at points equidistant from the axis, search coils with large effective areas could be designed readily to measure the radial field. With any non-symmetrical shape it would be necessary to construct search coils whose dimensions were small compared with the dimensions of the plate and the distances involved, so that the measured field could be assumed uniform throughout the search coil.

§ 2. EXPERIMENTAL ARRANGEMENT

The uniform field was produced by means of two large square loops of side 213.5 cm. joined in series and placed with their planes parallel and 116.3 cm. apart. This system, which forms a modified Helmholtz system, has been described by Rankine⁽⁴⁾ as a means of obtaining the most uniform field by means of square coils. If $2a$ is the side of the square and $2b$ the separation of the coils, the most uniform field is obtained if $a/b = 1.837$. In the system used $a/b = 1.836$. If the centre of the coil system is taken as the origin of coordinates, the axes Ox , Oy parallel to the sides of the coil and Oz perpendicular to them, then if H_0 is the field at the origin, the field at various points near the origin is as shown in table 1.

Table 1

Position	Field
(0, 0, 0)	H_0
($\pm 0.22a$, 0, 0)	$0.99902 H_0$
(0, $\pm 0.22a$, 0)	$0.99902 H_0$
($\pm \frac{0.22}{\sqrt{2}}a$, $\pm \frac{0.22}{\sqrt{2}}a$, 0)	$0.99952 H_0$
(0, 0, $\pm 0.22a$)	$0.99815 H_0$

It will be seen that over a circle of radius $0.22a$ (in this case 23.5 cm.) in the XOY plane, in which the disc lies, the field is constant to within one part in 1000. The maximum radius of the discs was 23.1 cm., and as the apparatus used was not capable of measuring to the above accuracy, the discs were assumed to be in a uniform field. The coil system was connected directly to the generator by twisted flex leads, which did not produce any appreciable magnetic field at the centre of the system. In the test, the current used was about 8 A. at 532 c./sec., giving a primary field of amplitude 0.062 oersted, or about 10 A. at 50 c./sec., giving a field of amplitude 0.077 oersted.

The apparatus used for measuring the field was originally designed for actual inductive prospecting⁽⁵⁾, and required only slight modification for small-scale work. The circuit for the work at 532 c./sec. is shown in figure 1. The search coil A , fixed in position relatively to the square Helmholtz coil system HH and threaded by the field due to it, supplies currents differing in phase by $\pi/2$ to the two potentiometers R , S . By varying the resistance X , the phase-difference between the currents in R

and the magnetic field at A can be changed until the e.m.f. set up in the search coil, placed in the normal uniform field of the Helmholtz system, is balanced on the scale R , the scale S being at its central zero. The instrument with this adjustment is direct-reading, and in the presence of a metal disc the readings on R give measures of the distorted field in phase and in quadrature with the applied field. For the work at 50 c./sec. it was necessary to change the constants of potentiometer, and owing to the difficulty of designing a suitable search coil to measure A at the lower frequency the phase-calibration could not be performed. This meant that the instrument was no longer direct-reading, but the in-phase and quadrature components of the distortion due to the discs could be readily calculated from the readings. Calculation showed that at both frequencies the field at the

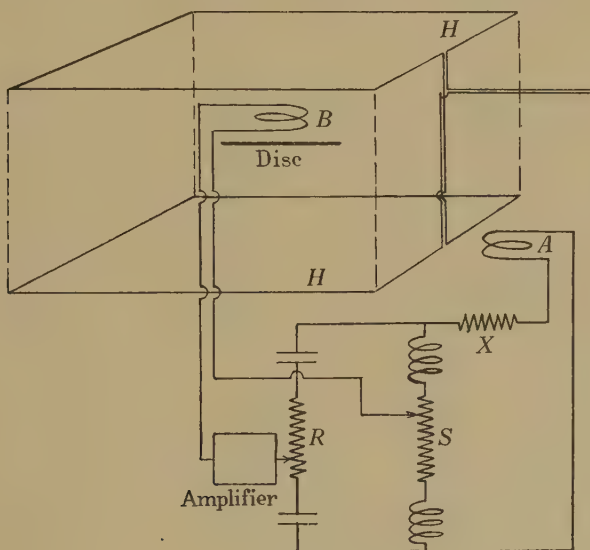


Figure 1.

of the square coil system due to the currents flowing through the fixed coil A is much less than 0.1 per cent of the main field and could be neglected in comparison with it.

The metal disc rested on three wooden levelling-screws passing through a wooden base, and its position was fixed in relation to the frame carrying the search coil by two wooden stops mounted on the base and contacting with the circumference of the disc. These stops consisted of suitable wooden screws passing through wooden blocks and they permitted the centre of the disc to be moved through a small range. The framework carrying the search coil was also mounted on the base and allowed the coil to be moved along the axis of the disc. In the construction of the mounting for the disc and search coil all metal was avoided so that the applied field was undistorted by the parts in question.

The field on the axis of the disc was measured by a small coil having 770 turns wound in a groove 0.6 cm. wide, 0.4 cm. deep and of mean radius 2.7 cm. The coil

was first placed in the position of the disc and the phase calibration performed, the reading on the in-phase scale giving a measure of H_0 , the applied field. At all other positions the readings were taken with and without the metal disc, and from them the distortion due to the disc was calculated as a fraction of the applied field.

The measurements of the radial field were made with suitable coils placed parallel to and coaxial with the disc and moved to different distances from the disc. The coils lay in two identically similar grooves, with a mean separation of 1 cm., cut in the same wooden former. Coils with the same number of turns were wound in each groove and connected in opposition, so that, when they were placed in a uniform field, the resultant e.m.f. induced in the system was zero. In any other field, if F_1 is the inward normal flux over the base, F_2 the outward normal flux over the top, and F_3 the outward normal flux over the curved surface, then, by Gauss's theorem,

$$F_1 - F_2 - F_3 = 0 \quad \text{or} \quad F_3 = F_1 - F_2.$$

As the coils are connected in opposition, the induced e.m.f. is a measure of $(F_1 - F_2)$, and hence the system measures F_3 directly. When the coil and disc are parallel and coaxial, F_3 will be due to the radial field of the currents in the disc at a distance from the axis equal to the mean radius of the coil. One advantage of these coils is that a slight displacement of the centre from the axis of the disc will not introduce any serious error, for one part of the coil will be moved into a greater radial field and another part into a weaker field. Since $\partial H_r / \partial r$ is the same for all points on the rim of the coil, where H_r is the radial field, the increase of flux on one side will be compensated by a decrease on the other.

It was found, in general, that coils constructed in this manner were not exactly astatic. Slight dissimilarities in the grooves, or small differences in the windings of the coils themselves, result in a small difference in the mean radii of the two component windings. Consequently the curved surface of the coil approximated to a section of a cone of small semivertical angle θ , rather than the section of a cylinder. If H_r and H_a are the radial field and the field parallel to the axis respectively, then

$$F_3 = (H_r \cos \theta + H_a \sin \theta) A \doteq (H_r + H_a \theta) A$$

when A is the effective area of the curved sides. When the coil is rotated through 180° about a diameter, the second term changes sign and the mean of the two observations eliminates the unwanted effect. The constants of the six coils used in the measurement of the radial field are given in table 2.

Table 2

Coil	Mean radius r (cm.)	No. of turns n	A (cm. ² $\times 10^4$)
<i>A</i>	4.6	450	1.31
<i>B</i>	7.1	300	1.35
<i>C</i>	11.3	200	1.41
<i>D</i>	14.8	150	1.40
<i>E</i>	18.8	120	1.41
<i>F</i>	22.6	100	1.42

A is the area of the curved surface of the coil and $= 2\pi rnh$, where h is the mean separation of the two windings. As before, the potentiometer has been calibrated with a coil of known effective area placed in the normal applied field, and the distortion due to the discs is expressed in terms of the applied field.

§ 3. EXPERIMENTAL RESULTS

The dimensions of the discs and their resistivities, obtained from measurements on specimens cut from the same sheet, are as shown in table 3.

Table 3

	Radius a (cm.)	Thickness d (cm.)	Resistivity ρ (e.m.u.)	d/ρ
Copper I	20.3	0.210	$2.94 \cdot 10^3$	$7.14 \cdot 10^{-5}$
Copper II	20.4	0.0475	$1.73 \cdot 10^3$	$2.75 \cdot 10^{-5}$
Brass	20.3	0.198	$6.56 \cdot 10^3$	$3.02 \cdot 10^{-5}$
Lead	20.3	0.342	$2.21 \cdot 10^4$	$1.55 \cdot 10^{-5}$
German silver I	23.1	0.0924	$2.47 \cdot 10^4$	$3.76 \cdot 10^{-6}$
German silver II	20.3	0.0924	$2.47 \cdot 10^4$	$3.76 \cdot 10^{-6}$
German silver III	17.8	0.0924	$2.47 \cdot 10^4$	$3.76 \cdot 10^{-6}$

The field on the axis of all seven discs was measured at 532 c./sec. and for the first five at 50 c./sec., but the radial field was obtained for copper I and lead at 532 c./sec. only. Typical examples of these fields are shown in figures 2, 3 and 4. In these diagrams the in-phase components are given by the continuous curves, the broken lines referring to the quadrature components. Some of the observations are shown on the curves to indicate the accuracy of the measurements, but in many cases, to avoid confusion, the observed values have been omitted. Figure 2 shows the in-phase components I_r and the quadrature components Q_r of the radial field, expressed as a fraction of the applied field H_0 , as measured with the coils in table 2 at various distances from the disc. It will be seen that the quadrature components are approximately between 0.3 to 0.5 of the in-phase components. Similar curves were obtained for copper I. In this case the maxima on the in-phase curves were displaced to a greater radial value and were larger than the maxima for the lead disc. The quadrature components were much smaller, the maximum measured value of Q_r/H_0 being 0.09, and in general they were about 0.1 of the in-phase components. With the aid of these and similar curves the complete radial fields have been depicted by lines of equal in-phase and equal quadrature component, figure 3. Figure 3*a*, in which the in-phase lines only are shown since the quadrature values were too small to be plotted accurately, refers to the copper, and figure 3*b* refers to the lead. It will be seen that, in general, the field at a given point is greater for the copper than for the lead, while the maxima for the copper are at a greater distance from the axis, illustrating the tendency for the current to concentrate nearer the rim of the better conductor.

Examples of the axial field are given in figure 4 for copper I, copper II and lead at 532 c./sec. and at 50 c./sec. Comparing the magnitude of the in-phase com-

ponents I_a/H_0 and the quadrature components Q_a/H_0 of the axial field for lead at 532 c./sec., we can see that they are of the same order as the corresponding ratio for the radial field, figure 2, a result which was confirmed by the measurements on copper I. This is to be expected, since outside the disc the components may be

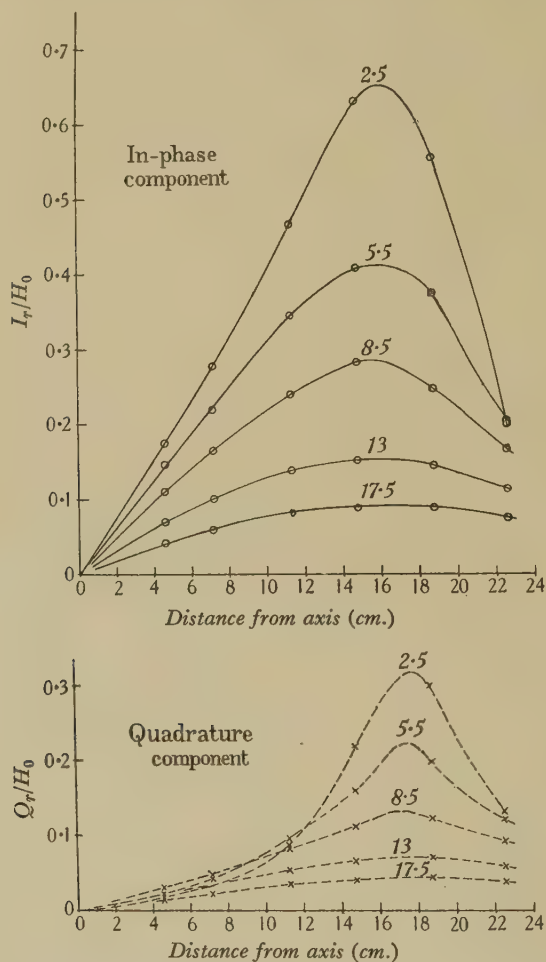


Figure 2. Radial field due to lead disc. The figures attached to the curves refer to the distance (cm.) from the disc.

Ω, r derived from a potential Ω which, on the axis and at a distance r from the disc, has the form

$$\Omega = \Sigma (Ar^n + B/r^{n+1}),$$

and at a point (r, θ, ϕ) off the axis

$$\Omega = (Ar^n + B/r^{n+1}) P_n(\cos \theta),$$

differing only by the introduction of the Legendre coefficient $P_n(\cos \theta)$. Accordingly, the factors controlling the magnitudes of the two components may be determined from an examination of the axial field only.

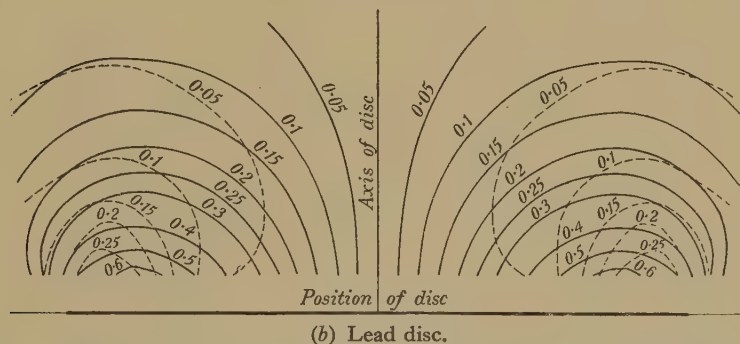
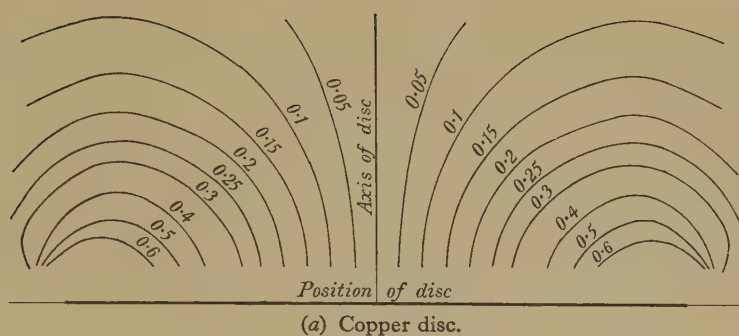


Figure 3. Radial field due to copper I and lead at 532 c./sec. The radius of I_r/H_0 and Q_r/H_0 are denoted by the figures attached to the curves.

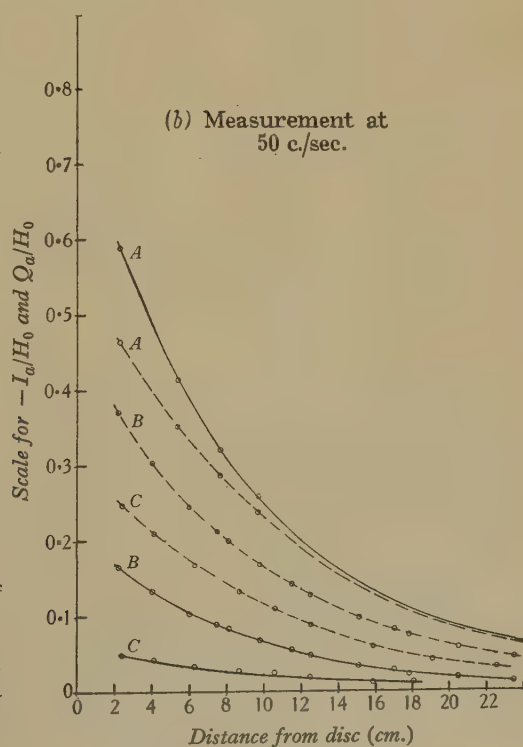
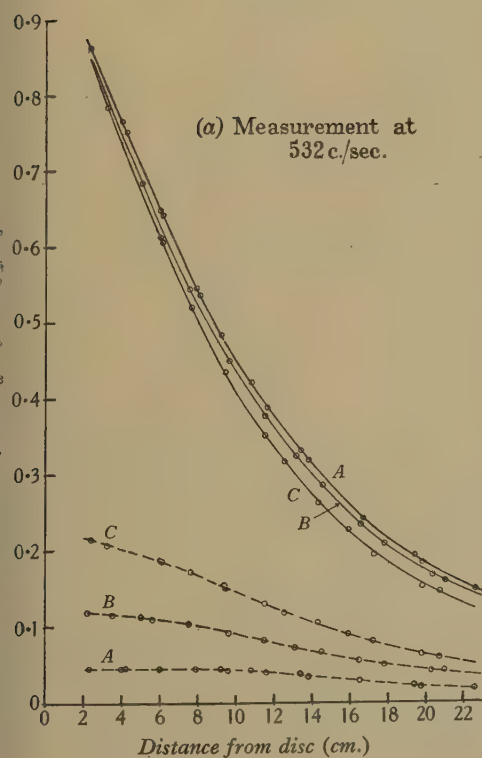


Figure 4. Axial field due to conducting discs, A, copper I; B, copper II; C, lead.

In the case of the axial field it will be seen that, at the high frequency, the in-phase component predominates, while at the lower frequency, and for the poorer conducting sheets such as copper II and lead, the quadrature component is larger than the in-phase component. In all cases the in-phase component for a given disc decreases considerably as the frequency changes from 532 c./sec. to 50 c./sec., and at a given frequency the component decreases with decreasing value of the ratio of thickness to resistivity. The values of this ratio for the three discs shown in figure 4 are for copper I, $7.14 \cdot 10^{-5}$; for copper II, $2.75 \cdot 10^{-5}$; and for lead, $1.51 \cdot 10^{-5}$. In the

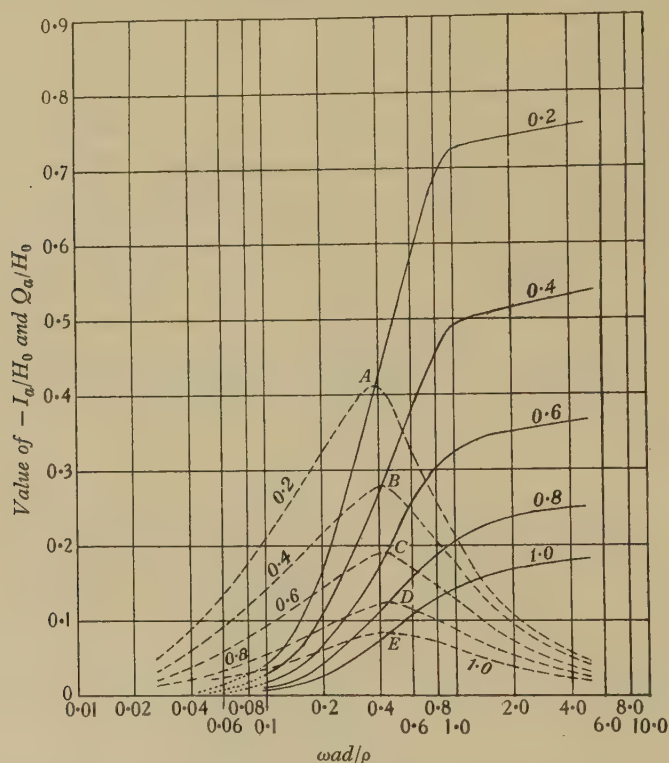


Figure 5. The value of z/a is indicated by the figures attached to the curves.

case of the quadrature components the relations are not quite so simple. The quadrature component is greater at the lower frequency for copper I, copper II and brass, but smaller for German silver I. In the case of lead, close to the disc the component is larger at the lower frequency, but at larger distances it is smaller. At the higher frequency the component increased as the ratio thickness/resistivity decreased, but at the lower frequency the conditions were reversed.

It was found that if for a given value of z/a the fields I_a/H_0 and Q_a/H_0 were plotted against $\omega a d/\rho$, where z is the distance from the disc and ω is 2π times the frequency, the points for all discs lie on smooth curves. The values derived from the experimental results for five different values of z/a are plotted in figure 5. For convenience, since $\omega a d/\rho$ for the discs used varies from 0.027 up to 4.86, a logarith-

mic scale has been used for this quantity. It will be seen that below 0.04 the in-phase component is negligible compared with the quadrature component. Between the values of 0.1 and 1.0 the in-phase component increases rapidly, and thereafter an increase in the parameter $\omega ad/\rho$ produces little effect, and presumably each curve tends to a limiting value corresponding to the effect of a perfect conductor. The quadrature curves rise to maxima as $\omega ad/\rho$ increases, and then fall away rapidly. It will be seen that the intersections *A*, *B*, *C*, *D* and *E* of corresponding in-phase and quadrature curves occur at the maxima of the quadrature curves. Thus, below 0.4 the quadrature components are greater and for sufficiently low values of the parameter the secondary field is entirely in quadrature with the applied field. Above 0.4 the in-phase field predominates, and for sufficiently large values of $\omega ad/\rho$ the distortion is entirely in-phase with the applied field.

§ 4. DISCUSSION OF RESULTS

These curves reproduce the same characteristics as other bodies when placed in a uniform field if the response is plotted against a suitable parameter. In the case of a sphere of radius *a*, the parameter^(2,6) is $\omega a^2/\rho$, while for a spherical shell of radius *r* and thickness *d* the parameter^(2,6) is $\omega ad/\rho$. Even with a simple loop it is easy to show that a field changing in the same manner will be obtained if the secondary field at a given point is plotted against ω/R , where *R* is the resistance of the circuit. Elementary considerations show that these features are to be expected for a conductor of given shape, when the distortion is plotted against a suitable parameter involving the resistivity, frequency and size of the body. The two factors controlling the magnitude and distribution of the induced currents in the conductor are the resistivity and the opposition to change of the magnetic field. For bodies of high resistivity or for low frequencies the resistivity is the important factor, and the induced currents are in phase with the induced e.m.f. $-j\omega N$, where *N* is the flux through a closed line of flow, and are proportional to $1/\rho$. For good conductors and high frequencies the second factor is the more important and roughly increases proportionally to the frequency. Consequently the induced currents are in quadrature with the induced e.m.f. and are practically independent of frequency, leading to in-phase fields which tend to a saturation value.

§ 5. APPLICATION OF THE PRINCIPLE OF SIMILITUDE

The parameter controlling the secondary field may be obtained more precisely from the electromagnetic equations. With electromagnetic units

$$\text{Curl } E = -\mu \dot{H},$$

$$\text{Curl } H = \frac{4\pi}{\rho} E,$$

where *E* and *H* are the electric and magnetic fields, μ is the permeability and ρ is the resistivity. These equations lead to

$$\frac{\partial^2 R}{\partial x^2} + \frac{\partial^2 R}{\partial y^2} + \frac{\partial^2 R}{\partial z^2} = \frac{4\pi\mu}{\rho} \frac{\partial R}{\partial t},$$

N

E, *H*, μ

R where R is any component of the electric or magnetic field. For bodies of similar shape, let α be the length of a line in the body, i.e. a measure of its linear dimensions, and let the coordinates be expressed in terms of this length. Thus

$$x = \xi\alpha, \quad y = \eta\alpha, \quad z = \zeta\alpha,$$

and hence
$$\frac{\partial^2 R}{\partial \xi^2} + \frac{\partial^2 R}{\partial \eta^2} + \frac{\partial^2 R}{\partial \zeta^2} = \frac{4\pi\mu\alpha^2}{\rho} j\omega R \quad \dots\dots(1),$$

since, in the case of alternating fields, when a steady state has been reached, $\partial/\partial t$ may be replaced by the operator $j\omega$. Consequently

$$R = F\left(\frac{4\pi\mu\alpha^2 j\omega}{\rho}, \xi, \eta, \zeta\right) \quad \dots\dots(2),$$

and the parameter controlling the response is $\omega\mu\alpha^2/\rho$, corresponding to $\omega\alpha^2/\rho$ which obtains for the case of the sphere. Equation (2) involves the principle of similitude first pointed out by C. V. Drysdale⁽⁷⁾, for to reproduce the field in a particular case on a different scale $\omega\mu\alpha^2/\rho$ must be a constant. Since the wave-length λ of an electromagnetic disturbance in a medium is $\sqrt{(\rho/2\pi\omega\mu)}$, the principle of similitude requires that the wave-length of the disturbance shall be changed by the same factor as the other linear dimensions.

Equation (2) is not directly applicable to the case of the discs here used because they are not bodies of similar shape, i.e. a/d is not a constant. For laminae of the same shape but differing in thickness d and in α , a measure of the surface dimensions, the following equation holds outside the lamina:

$$\frac{\partial^2 R}{\partial \xi^2} + \frac{\partial^2 R}{\partial \eta^2} + \frac{\partial^2 R}{\partial \zeta^2} = 0 \quad \dots\dots(3),$$

in virtue of equation (1), since $\rho = \infty$. If the lamina lies in the XOY plane it can be shown that⁽⁸⁾

$$\frac{4\pi d}{\rho} \cdot \frac{\partial H_{z1}}{\partial t} = \frac{4\pi d}{\rho} \cdot \frac{\partial H_{z2}}{\partial t} = \left| \frac{\partial H_z}{\partial z} \right|_1^2,$$

where the suffixes 1 and 2 refer to points close to the boundary on each side of the sheet. Hence, since $z = \alpha\zeta$ and $\frac{\partial}{\partial t} = j\omega$,

$$\frac{4\pi j\omega\alpha d}{\rho} H_{\zeta 1} = \frac{4\pi j\omega\alpha d}{\rho} H_{\zeta 2} = \left| \frac{\partial H_\zeta}{\partial \zeta} \right|_1^2 \quad \dots\dots(4),$$

from which, in combination with equations (3) and (4); it would appear that the field is of the form

$$R = F\left(\frac{4\pi j\omega\alpha d}{\rho}, \xi, \eta, \zeta\right),$$

which agrees with the experimental results obtained with the discs, and with the result quoted for the spherical shell. One feature of the above analysis is that the exact nature of the exciting field is not specified and thus the general results can be applied to bodies not in uniform fields.

§ 6. CONCLUSIONS

Three inferences of great practical importance to the application of the inductive methods of locating well-conducting subterranean bodies may be drawn from these results. In the first case there is no simple phase relation between the secondary field and the applied field, and the field instruments must be capable of dealing with all phase conditions. With the resistivities and dimensions of bodies available in practice, it is probable that only the smaller values of $\omega ad/\rho$ are important and, although in this range the quadrature components predominate, the in-phase component may be an appreciable fraction of the total field. It also appears that, for a body of given surface dimensions, exactly the same field will be obtained for all combinations of resistivity and thickness as long as the ratio remains constant. Thus a bed of clay of resistivity 500 Ω .-cm. and thickness 100 cm. will be indistinguishable from a copper-sulphide body of resistivity 100 Ω .-cm. and thickness 20 cm.

The fact that the secondary field increases with frequency does not imply that, in the practical case, a body will be more readily detected if a higher frequency is used, for another factor enters into the problem. The surrounding rocks have a finite resistivity, usually much greater than the resistivity of a sulphide body, and accordingly induced currents are set up in those rocks, giving rise at the surface to a secondary field which forms a background on which local effects are superimposed. The primary field is thus decreased by absorption occurring in the rocks that lie between the body and the surface, and the absorption increases as the resistivity decreases or the frequency increases. For the secondary field at the surface due to the body there are two opposing factors, the primary field decreasing with frequency and the response increasing with frequency. Consequently there is an optimum frequency for a given body which will yield the best results. An increase in the frequency beyond the optimum value will result in a smaller indication on an increased background, while a decrease in the frequency will reduce both the local anomaly and the background, the former being reduced by the greater factor. The optimum frequency will decrease with increasing depth of the body and also with decrease of resistivity of the intervening medium. In the case of a large surface conductivity, the optimum frequency may be so small that the field at the surface due to the body will be negligible compared with the applied field. Under these conditions the inductive method is at a marked disadvantage, which it shares with other methods employing alternating currents.

§ 7. ACKNOWLEDGMENTS

In conclusion I wish to thank Prof. A. O. Rankine for the interest he has taken in this work and also the Department of Scientific and Industrial Research, whose grant to the Applied Geophysics Department of the Royal College of Science rendered this work possible.

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AN OPTICAL CALIBRATION PROBLEM

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ABSTRACT. Suitable measures are obtained for the uncertainty, corresponding to a fixed error of phase, in the object-image relation of a symmetrical optical instrument. For a thin lens with its aperture stop in contact with the lens the uncertainty is proportional to the distance between the object and the image. The formulae are utilized to determine the most accurate values of the coefficients in the object-image relation from observations including many pairs of co-ordinates.

The results given by the phase criterion, unlike those derived by a purely geometrical treatment, are unaltered if the object and image spaces are interchanged.

IN the course of optical experiments it is sometimes required to determine the connexion between conjugate points for part of the optical train without disturbing this portion of the apparatus. The procedure followed is to attach to the apparatus scales on which corresponding positions u , u' of an object and its image can be read. These observations have then to be fitted to a formula of the type

$$Auu' - Bu' - Cu + D = 0 \quad \dots\dots(1).$$

Three pairs of points suffice to give a solution, but it is usual to observe a greater number. In general each set of three will then yield different values of the ratios $B : C : D$, and the method of selecting mean values deserves attention. Obviously comparatively little weight can be assigned to determinations from close sets of points. For such sets the minors of

$$\begin{vmatrix} u_1 u_1' & u_1' & u_1 & 1 \\ u_2 u_2' & u_2' & u_2 & 1 \\ u_3 u_3' & u_3' & u_3 & 1 \end{vmatrix}$$

be small, but it does not follow that we shall reach a satisfactory result by merely adding corresponding minors, for by this procedure if any observation is included with u or u' indefinitely great this single observation alone would determine the ratio of B or C to A irrespective of all the others. From the nature of the arrangement we cannot avoid this difficulty by adopting an expression which involves only the reciprocals of u and u' . Indeed the fact that a small change in one scaling may correspond to a large change in the other should put us on our guard against accepting any treatment which does not take into account the physics of the problem.

It is now widely recognized that the correct measure of errors of focus is the difference of path, as utilized in the late Lord Rayleigh's treatment of somewhat similar problems. In the question we are considering it may be assumed that the same path differences will be obtained by comparing axial and marginal paths.

If the inclination of the extreme rays to the axis is of moderate magnitude, and u and u' are assumed to increase as the distances from the lens of the object and image respectively increase,* the marginal path will exceed the axial path by T ,† where

$$2AT = (B - uA)(M^2 + N^2) - 2(MM' + NN') + (C - u'A)(M'^2 + N'^2) \dots (2),$$

and M , N and M' , N' are the direction cosines of a marginal ray with respect to axes perpendicular to the axis of the system. The corresponding intersection distances in the u and u' planes of this ray are given by the equations

$$\begin{aligned} Ay &= (B - uA)M - M', & Ay' &= M - (C - u'A)M', \\ Az &= (B - uA)N - N', & Az' &= N - (C - u'A)N'. \end{aligned}$$

Similarly if the aperture is limited by a stop corresponding to one of the scale readings $u=s$, $u'=s'$, and the intersection points in the stop plane are η , ζ or η' , ζ' , we shall have

$$\begin{aligned} A\eta &= (B - sA)M - M', & A\eta' &= M - (C - s'A)M', \\ A\zeta &= (B - sA)N - N', & A\zeta' &= N - (C - s'A)N'. \end{aligned}$$

Considering now light from an object point on the axis, so that $y=z=0$, we obtain

$$\begin{aligned} M &= \frac{\eta}{u-s} = \frac{-\eta'}{Aus' - Bs' - Cu + D} = \frac{M'}{B - uA}, \\ N &= \frac{\zeta}{u-s} = \frac{-\zeta'}{Aus' - Bs' - Cu + D} = \frac{N'}{B - uA}, \end{aligned}$$

where we have assumed the relation $BC - AD = 1$ in deriving the values involving η' and ζ' . Substituting these values of the direction cosines in (2) we obtain

$$\begin{aligned} \frac{2T}{\eta^2 + \zeta^2} &= \frac{(B - uA)(Auu' - Bu' - Cu + D)}{(u-s)^2}, \\ \text{or} \quad \frac{2T}{\eta'^2 + \zeta'^2} &= \frac{(B - uA)(Auu' - Bu' - Cu + D)}{(Aus' - Bs' - Cu + D)^2}. \end{aligned}$$

Both these equations may be expressed in a single form. If we put

$$Auu' - Bu' - Cu + D = d,$$

$-d$ is the optical interval between the planes selected (with some small error) as corresponding conjugate planes. If the stop is in the object space, $u-s$ is the separation between the object and the stop plane, and if the stop is in the image space $-d_s$ is the corresponding optical interval, where $Aus' - Bs' - Cu + D = d_s$. In the first case the real and the optical intervals are identical; we may accordingly denote either of these optical intervals by $-d_s$. Moreover $B - uA$ is the reciprocal of the magnification m which the object undergoes in the system we are considering. We therefore have in all cases

$$\frac{2T}{r^2} = \frac{d}{md_s^2} \dots\dots (3),$$

where r is the radius of the effective stop.

* The conventions are those of Group II, Case 1, described in the *Report on the Teaching of Geometrical Optics*, The Physical Society, 1934.

† Hamilton's notation for one of his auxiliary characteristic functions is adopted.

The asymmetry in this formula is due to our having definite knowledge of agreement of phase at the object, but not in the approximate image plane. If however we neglect errors in focus except in the factor d itself, we can immediately convert (3) into the symmetrical form

$$\frac{2T}{rr'} = \frac{2T}{\eta\eta' + \zeta\zeta'} = -\frac{d}{d_s d_s'} \quad \dots\dots(4),$$

where $-d_s'$ is the optical interval between the image plane and the image of the real stop plane, i.e. d_s' has one of the values $-(u'-s')$, $Au's-Bu'-Cs+D$, the choice depending upon whether the real stop is in the object or the image space.

An important special case of (4) arises when the effective stop is in a principal plane. We then have $r'=r$, the relation connecting conjugate points is

$$A + \frac{1}{d_s} + \frac{1}{d_s'} = 0,$$

and the formula reduces to

$$\frac{2T}{Ar^2} = -\frac{d}{\mathcal{D}} \quad \dots\dots(5),$$

where \mathcal{D} is the overall distance between object and image planes less the actual distance between the principal planes. For a thin lens the principal planes are coincident, and for many systems their separation is negligible, so that \mathcal{D} may be taken with sufficient accuracy to be the distance apart of the object and image.

We see therefore that, corresponding to a given standard of accuracy in focussing, the tolerance in d is proportional to md_s^2 , or with sufficient accuracy to $d_s d_s'$, and that it will often be the case, with the stop in or near to a principal plane, that the tolerance is proportional to \mathcal{D} , the distance apart of the object and image.

A practical procedure is to compute provisional values of A, B, C, D from a mean and the two extreme positions of object and image. With these values of the constants compute values of d for all the observations, and then evaluate either md_s^2 or $d/d_s d_s'$ or d/\mathcal{D} . If the distribution of these quantities is not systematic as regards sign and the largest positive and largest negative values are of equal magnitude, the values of A, B, C, D obtained may be accepted as satisfactory. Otherwise from these quantities we pick out four which are judged to have the largest outstanding errors from a mean curve, these being alternately positive and negative as increases.* Distinguish these outstanding observations by the suffixes 1, 2, 3, 4. Assume, for the purpose of illustration, that \mathcal{D} is a suitable measure of the tolerance to be permitted, and that $\mathcal{D}_1, \mathcal{D}_2, \mathcal{D}_3, \mathcal{D}_4$ are the values of \mathcal{D} for the four observations. Then the equation which fits the observations best is

$$\begin{vmatrix} uu' & u' & u & 1 & 0 \\ u_1 u_1' & u_1' & u_1 & 1 & \mathcal{D}_1 \\ u_2 u_2' & u_2' & u_2 & 1 & -\mathcal{D}_2 \\ u_3 u_3' & u_3' & u_3 & 1 & \mathcal{D}_3 \\ u_4 u_4' & u_4' & u_4 & 1 & -\mathcal{D}_4 \end{vmatrix} = 0 \quad \dots\dots(6).$$

* For a discussion of the principle adopted see "The mid-course method of fitting a parabolic formula of any order to a set of observations", *Proc. phys. Soc.* 46, 560 (1934).

When the best relative values of A, B, C, D have been obtained their absolute values, if required, are found by dividing each by $(BC - AD)^{\frac{1}{2}}$. The resolution of the ambiguity of sign offers no difficulty in practice. If the scales are arranged differently it may happen that the dividing factor will be $(AD - BC)^{\frac{1}{2}}$. In any event the factor is real, and the sign will be chosen to give the correct sign for A . For details see the reference on p. 76.

$\mathcal{D}_1, \mathcal{D}_2, \mathcal{D}_3$ and \mathcal{D}_4 may be regarded as weights attached to the determinations of A, B, C, D when the pairs of points 1, 2, 3, 4 respectively are omitted. The determinant (E say) obtained by deleting the first row and last column from (6) measures the magnitude of the outstanding errors. For if we denote by A_p, B_p, C_p, D_p the coefficients found when points p are omitted, alternations of sign being avoided, we have

$$E = \begin{pmatrix} u_1 u_1' & u_1' & u_1 & 1 \\ u_2 u_2' & u_2' & u_2 & 1 \\ u_3 u_3' & u_3' & u_3 & 1 \\ u_4 u_4' & u_4' & u_4 & 1 \end{pmatrix} \begin{pmatrix} A_1 & -A_2 & A_3 & -A_4 \\ -B_1 & B_2 & -B_3 & B_4 \\ -C_1 & C_2 & -C_3 & C_4 \\ D_1 & -D_2 & D_3 & -D_4 \end{pmatrix}$$

$$\text{and } \frac{A}{\Sigma \mathcal{D}_p A_p} = \frac{B}{\Sigma \mathcal{D}_p B_p} = \frac{C}{\Sigma \mathcal{D}_p C_p} = \frac{D}{\Sigma \mathcal{D}_p D_p} = \frac{A u_p u_p' - B u_p' - C u_p + D}{-(-)^p E \mathcal{D}_p}$$

$$= \frac{1}{(\Sigma \mathcal{D}_p B_p \Sigma \mathcal{D}_p C_p - \Sigma \mathcal{D}_p A_p \Sigma \mathcal{D}_p D_p)^{\frac{1}{2}}} = \frac{1}{(\Sigma \mathcal{D}_p \Sigma \mathcal{D}_p \Delta_p - \Sigma \mathcal{D}_p \mathcal{D}_q \Delta_{pq})^{\frac{1}{2}}} \dots (7),$$

where

$$\Delta_p = B_p C_p - A_p D_p$$

and

$$\Delta_{pq} = (B_p - B_q)(C_p - C_q) - (A_p - A_q)(D_p - D_q).$$

Δ_p can be expressed as the product of six factors, and Δ_{pq} as the product of four factors, but it will usually be unnecessary to evaluate them directly.

The quality of the observations can be determined from the values of T when the final values of A, B, C, D are inserted in one of the equations (3), (4) or (5). According to Lord Rayleigh T should lie within the limits $\pm \lambda/4$ for sensibly perfect definition, where λ is the equivalent wave-length of the light used. In our problem we interpret this tolerance as fixing the limits of sensibly perfect focussing.

It may be observed that, as with other questions of this class, the results reached by means of limits depending on path differences disagree with those derived geometrically by assuming that the definition will appear satisfactory if the rays intersect an image plane in an area less than a fixed limiting size. It is not difficult to show that this assumption leads to tolerances in d proportional to d_s . It should be noted that, unlike the results given earlier, this conclusion is essentially unsymmetrical as regards the object and image spaces, so that if object and image are interchanged the distribution of tolerances on this basis will be altered.

ON THE COMBINATION OF OBSERVATIONAL DATA

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ABSTRACT. A method is devised for solving the following problem: Given m curves derived by m different experimenters to describe the same physical process, how are these to be combined into one unique curve? Formulae are developed that enable the ordinates of the combined curve to be calculated simply from those of the constituent members.

SUPPOSE that m experimenters each separately investigating a particular process produce m sets of data or m curves each purporting to describe the same phenomenon quantitatively. How are these separate curves to be combined? Can any criterion be developed that enables us to decide what weight to attach to each of the individual members of the system in combining them?

It seems clear that such weights must be associated with the extent to which each one of the sets correlates as a whole with every other set, in addition to the extent to which any particular reading is in partial agreement with other corresponding readings. A direct and unconditioned use of the method of least squares would not take these considerations into account. We commence with the case of two sets of data.

(1) Let (A_1, \dots, A_n) and (B_1, \dots, B_n) be two sets of observations obtained by two different experimenters to represent variations in the same phenomena at positions x_1, \dots, x_n not necessarily evenly spaced. We assume that no errors arise in determining x_1, \dots, x_n , that the values of the A s and B s are almost entirely determined by the nature of the subject-matter investigated, and that the differences between A_1 and B_1 , A_2 and B_2 , etc. arise only from experimental errors. It follows that the A and B series should be highly correlated. The problem is to derive from these observations a third series Y_1, Y_2, \dots, Y_n at x_1, x_2, \dots, x_n which *correlates most highly with* (A) and (B). This last phrase is taken to mean that if r_{ay} and r_{by} be the correlation coefficients between the A s and the Y s and between the B s and the Y s respectively, when the Y s are to be chosen to make a homogeneous symmetrical function a maximum.

(2) Let M_A, M_B, M_Y be the arithmetic means of the A s, the B s and the Y s. If α_s, β_s and η_s are deviations of A_s, B_s and Y_s each from its mean, then

$$\sum_1^n \alpha_s = \sum_1^n \beta_s = \sum_1^n \eta_s = 0,$$

$$r_{ab} = \frac{\sum \alpha_s \beta_s}{\sqrt{(\sum \alpha_s^2 \cdot \sum \beta_s^2)}}, \quad r_{ay} = \frac{\sum \alpha_s \eta_s}{\sqrt{(\sum \alpha_s^2 \cdot \sum \eta_s^2)}}, \quad r_{by} = \frac{\sum \beta_s \eta_s}{\sqrt{(\sum \beta_s^2 \cdot \sum \eta_s^2)}}.$$

 A_n, B_n x_n Y_n r_{ay}, r_{by} M_A, M_B, M_Y $\alpha_s, \beta_s, \eta_s$

It will simplify our notation if we write

$$a_s, b_s, y_s \quad \frac{\alpha_s}{\sqrt{\sum \alpha_s^2}} = a_s, \quad \frac{\beta_s}{\sqrt{\sum \beta_s^2}} = b_s, \quad \frac{\eta_s}{\sqrt{\sum \eta_s^2}} = y_s.$$

Then

$$\begin{aligned} \sum_1^n a_s &= \sum_1^n b_s = \sum_1^n y_s = 0, \\ \sum_1^n a_s^2 &= \sum_1^n b_s^2 = \sum_1^n y_s^2 = 1, \\ r_{ab} &= \sum_1^n a_s b_s; \quad r_{ay} = \sum_1^n a_s y_s; \quad r_{by} = \sum_1^n b_s y_s. \end{aligned}$$

Thus the problem of determining the set (Y) that correlates most highly with the sets (A) and (B) can be expressed in terms of the sets (y), (a) and (b).

(3) We examine in the first place how far the set (y_1, \dots, y_n) can be determined to make $F(r_{ay}, r_{by})$ a maximum where F is a given continuous homogeneous function of degree N .

For this we require

$$\delta F = \frac{\partial F}{\partial r_{ay}} \delta r_{ay} + \frac{\partial F}{\partial r_{by}} \delta r_{by} = 0 \quad \text{.....(1),}$$

where

$$\delta r_{ay} = \sum a_s \delta y_s \quad \text{and} \quad \delta r_{by} = \sum b_s \delta y_s \quad \text{.....(2).}$$

Thus inserting (2) in (1) we require

$$\sum_1^n \left(a_s \frac{\partial F}{\partial r_{ay}} + b_s \frac{\partial F}{\partial r_{by}} \right) \delta y_s = 0 \quad \text{.....(3).}$$

In addition, from the restrictive conditions on y , we have

$$\sum_1^n y_s \delta y_s = 0, \quad \sum_1^n \delta y_s = 0 \quad \text{.....(4).}$$

Combining (3) and (4) in the usual way we find that

$$\lambda, \mu \quad \sum_1^n \left(a_s \frac{\partial F}{\partial r_{ay}} + b_s \frac{\partial F}{\partial r_{by}} + \lambda y_s + \mu \right) \delta y_s = 0,$$

where λ and μ are constants to be determined.

Equating coefficients of δy_s to zero we have

$$a_s \frac{\partial F}{\partial r_{ay}} + b_s \frac{\partial F}{\partial r_{by}} + \lambda y_s + \mu = 0 \quad (s = 1, \dots, n) \quad \text{.....(5).}$$

Summing the set (5) and remembering that

$$\sum a_s = \sum b_s = \sum y_s = 0, \text{ we deduce that } \mu = 0.$$

Multiplying (5) by y_s , summing and noting that

$$\sum a_s y_s = r_{ay}, \quad \sum b_s y_s = r_{by}, \quad \sum y_s^2 = 1,$$

we find

$$r_{ay} \frac{\partial F}{\partial r_{ay}} + r_{by} \frac{\partial F}{\partial r_{by}} + \lambda = 0.$$

Thus, since F is a homogeneous function of N th degree, by Euler's theorem

$$\lambda = -NF.$$

Accordingly (5) takes the form

$$a_s \frac{\partial F}{\partial r_{ay}} + b_s \frac{\partial F}{\partial r_{by}} = y_s NF \quad (s = 1, \dots, n) \quad \dots\dots(6).$$

Multiplying (6) by a_s and b_s respectively and summing we obtain

$$\left. \begin{aligned} \frac{\partial F}{\partial r_{ay}} + r_{ab} \frac{\partial F}{\partial r_{by}} &= r_{ay} NF \\ r_{ab} \frac{\partial F}{\partial r_{ay}} + \frac{\partial F}{\partial r_{by}} &= r_{by} NF \end{aligned} \right\} \quad \dots\dots(7).$$

Equations (6) and (7) between them serve to determine r_{ay} , r_{by} and y_s .

(4) Eliminating NF , $\frac{\partial F}{\partial r_{ay}}$ and $\frac{\partial F}{\partial r_{by}}$ between (6) and (7) we have

$$\begin{vmatrix} a_s & b_s & y_s \\ 1 & r_{ab} & r_{ay} \\ r_{ab} & 1 & r_{by} \end{vmatrix} = 0$$

$$y_s [1 - r_{ab}^2] = a_s [r_{ay} - r_{ab} r_{by}] + b_s [r_{by} - r_{ab} r_{ay}] \quad \dots\dots(8).$$

Again associating Euler's identity

$$r_{ay} \frac{\partial F}{\partial r_{ay}} + r_{by} \frac{\partial F}{\partial r_{by}} = NF$$

with (7) and eliminating F we have

$$\begin{vmatrix} 1 & r_{ab} & r_{ay} \\ r_{ab} & 1 & r_{by} \\ r_{ay} & r_{by} & 1 \end{vmatrix} = 0$$

$$(1 - r_{ab}^2)(1 - r_{ay}^2) = (r_{by} - r_{ab} r_{ay})^2 \quad \dots\dots(9).$$

For our purpose we shall be interested in the case where F is symmetrical in r_{ay} and r_{by} , in which case (7) implies that

$$r_{ay} = r_{by}.$$

Equation (9) then gives

$$r_{ay} = r_{by} = \sqrt{\frac{1 + r_{ab}}{2}} \quad \dots\dots(10),$$

$$\text{and (8)} \quad y_s = (a_s + b_s) / \sqrt{2(1 + r_{ab})} \quad \dots\dots(11).$$

Since it can easily be shown that $|r_{ab}| \leq 1$ and r_{ab} is positive for those cases with which we are concerned, it follows that y_s is in general slightly greater than the mean a_s and b_s .

We have now to reinterpret these results in terms of the original set of data:

$$\text{Observed values } \begin{cases} x_1, & x_2, & x_3, \dots, x_n \\ A_1, & A_2, & A_3, \dots, A_n \\ B_1, & B_2, & B_3, \dots, B_n. \end{cases}$$

$$(5) \text{ Now } Y_s = M_Y + \eta_s = M_Y + \gamma y_s \quad \dots\dots(12), \quad \gamma$$

where M_Y and γ are still unknown.

$$\text{Also } A_s = M_A + \alpha_s, \quad B_s = M_B + \beta_s.$$

We propose to determine M_Y and γ by the method of least squares.

Thus we require

$$\sum_1^n [(Y_s - A_s)^2 + (Y_s - B_s)^2],$$

$$\text{i.e.} \quad \sum_1^n [(M_Y + \gamma y_s - M_A - \alpha_s)^2 + (M_Y + \gamma y_s - M_B - \beta_s)^2],$$

to be a minimum for variations in M_Y and γ . This leads easily to the two equations

$$M_Y = \frac{1}{2} (M_A + M_B) \quad \dots\dots(13),$$

and

$$2\gamma \sum_1^n y_s^2 = \sum_1^n \alpha_s y_s + \sum_1^n \beta_s y_s,$$

or since

$$r_{ay} = r_{by},$$

or

$$2\gamma = r_{ay} (\sqrt{\sum_1^n \alpha_s^2} + \sqrt{\sum_1^n \beta_s^2}),$$

$$\gamma = \frac{\sqrt{n}}{2} r_{ay} [\sigma_A + \sigma_B] \quad \dots\dots(14),$$

σ_A, σ_B

where σ_A and σ_B are the standard deviations of the A and B series respectively.

Thus $Y_s = M_Y + \gamma y_s$

$$\begin{aligned} &= \frac{1}{2} (M_A + M_B) + \frac{\sqrt{n}}{2} r_{ay} [\sigma_A + \sigma_B] \frac{a_s + b_s}{\sqrt{2(1 + r_{ab})}} \\ &= \frac{1}{2} (M_A + M_B) + \frac{\sqrt{n}}{4} [\sigma_A + \sigma_B] \left[\frac{\alpha_s}{\sqrt{\sum \alpha^2}} + \frac{\beta_s}{\sqrt{\sum \beta^2}} \right] \\ &= \frac{1}{2} (M_A + M_B) + \frac{1}{4} [\sigma_A + \sigma_B] \left[\frac{\alpha_s}{\sigma_A} + \frac{\beta_s}{\sigma_B} \right] \quad \dots\dots(15), \end{aligned}$$

where M_A and M_B are the means of the A s and B s respectively, and the α s and β s are the deviations of these values from their means so that

$$A_s = M_A + \alpha_s, \quad B_s = M_B + \beta_s.$$

Accordingly all the constants in the calculation of the series Y that correlates most highly with the two experimentally determined series A and B have now been determined.

Turning now to the general case of m sets (A), (B), (C), . . . we proceed with the analysis as before. Corresponding to equation (7) associated with Euler's identity we have

$$\frac{\partial F}{\partial r_{ay}} + r_{ab} \frac{\partial F}{\partial r_{by}} + r_{ac} \frac{\partial F}{\partial r_{cy}} = r_{ay} NF \quad \dots\dots(16),$$

$$r_{ab} \frac{\partial F}{\partial r_{ay}} + \frac{\partial F}{\partial r_{by}} + r_{bc} \frac{\partial F}{\partial r_{cy}} = r_{by} NF \quad \dots\dots(17),$$

$$r_{ac} \frac{\partial F}{\partial r_{ay}} + r_{bc} \frac{\partial F}{\partial r_{by}} + \frac{\partial F}{\partial r_{cy}} = r_{cy} NF \quad \dots\dots(18),$$

$$r_{ay} \frac{\partial F}{\partial r_{ay}} + r_{by} \frac{\partial F}{\partial r_{by}} + r_{cy} \frac{\partial F}{\partial r_{cy}} = NF \quad \dots\dots(19).$$

Also in the same way corresponding to equation (8)

$$\begin{vmatrix} a_s & b_s & c_s & y_s \\ \mathbf{I} & r_{ab} & r_{ac} & r_{ay} \\ r_{ab} & \mathbf{I} & r_{bc} & r_{by} \\ r_{ac} & r_{bc} & \mathbf{I} & r_{cy} \end{vmatrix} = 0 \quad \dots\dots(20).$$

Equations (16), (17) and (18) serve to determine r_{ay} , r_{by} , r_{cy} in any given case and as before equation (21) gives y_s as a linear combination of a_s , b_s and c_s . Unlike the case of two sets A and B , the precise values of these correlation coefficients for a larger number of sets appear to depend on the nature of the function F . The case of a linear function however leads easily to a solution. Here we have the sets of observed values (A) , (B) , (C) , ... and we have to determine the set (Y) to make the correlation function

$$F = r_{ay} + r_{by} + r_{cy} + \dots \quad \dots\dots(21)$$

maximum.

Equations (16), (17) and (18) lead to

$$r_{ay} = (r_{aa} + r_{ab} + r_{ac} + \dots) / \sqrt{\sum_{p,q=a,b,c,\dots} \sum r_{pq}} \quad \dots\dots(22),$$

where

$$r_{aa} = r_{bb} = \dots = \mathbf{I},$$

from which it easily follows that equation (20) leads to

$$y_s = (a_s + b_s + c_s + \dots) / \sqrt{\sum_{p,q=a,b,c,\dots} \sum r_{pq}} \quad \dots\dots(23).$$

Once more writing

$$Y_s = M_Y + \eta_s = M_Y + \gamma y_s,$$

where M_Y is the mean of the terms in the Y set and applying the method of least squares we easily find, if there are m sets (A) , (B) , (C) , ..., that

$$M_Y = \frac{\mathbf{I}}{m} (M_A + M_B + M_C + \dots) \quad \dots\dots(24),$$

and

$$\begin{aligned} m\gamma &= \sum_1^n \alpha_s y_s + \sum_1^n \beta_s y_s + \dots \\ &= \sqrt{n} [r_{ay}\sigma_A + r_{by}\sigma_B + \dots] \quad \dots\dots(25). \end{aligned}$$

Thus finally

$$\begin{aligned} Y_s &= M_Y + \gamma y_s \\ &= \frac{\mathbf{I}}{m} [M_A + M_B + M_C + \dots] \\ &\quad + \frac{\sqrt{n}}{m} [r_{ay}\sigma_A + r_{by}\sigma_B + \dots] [a_s + b_s + c_s + \dots] / \sqrt{\sum_{p,q=a,b,c,\dots} \sum r_{pq}} \\ &= \frac{\mathbf{I}}{m} [M_A + M_B + M_C + \dots] \\ &\quad + \frac{\mathbf{I}}{m} [r_{ay}\sigma_A + r_{by}\sigma_B + \dots] \left[\frac{\alpha_s}{\sigma_A} + \frac{\beta_s}{\sigma_B} + \dots \right] / \sqrt{\sum_{p,q=a,b,c,\dots} \sum r_{pq}} \quad \dots\dots(26). \end{aligned}$$

In the case of three sets (*A*), (*B*) and (*C*), for example, this may be written

$$Y_s = \frac{1}{3} (M_A + M_B + M_C) + \frac{1}{3} \left(\frac{\alpha_s}{\sigma_A} + \frac{\beta_s}{\sigma_B} + \frac{\gamma_s}{\sigma_C} \right) \frac{\sigma_A + \sigma_B + \sigma_C + r_{ab}(\sigma_A + \sigma_B) + r_{bc}(\sigma_B + \sigma_C) + r_{ca}(\sigma_C + \sigma_A)}{3 + 2(r_{ab} + r_{bc} + r_{ca})} \dots (27).$$

We note that if all the sets show the same standard deviation, then the value of *Y* at each position is simply the mean of the separate ordinates.

The following table indicates the steps in the calculation and checks for *n* observations in each set.

Observations:

$\begin{array}{c} A_s \\ \hline \hline \end{array}$	$\begin{array}{c} \alpha_s = M_A - A_s \\ \hline \hline \end{array}$	$\begin{array}{c} \alpha_s^2 \\ \hline \hline \end{array}$	$\begin{array}{c} \alpha_s / \sigma_A \\ \hline \hline \end{array}$		
$\begin{array}{c} \Sigma \div n \\ = M_A \end{array}$	$\Sigma = 0$	$\begin{array}{c} \Sigma \div n \\ = \sigma_A^2 \end{array}$	$\Sigma = 0$	$\sigma_A = \dots$	
$\begin{array}{c} B_s \\ \hline \hline \end{array}$	$\begin{array}{c} \beta_s = M_B - B_s \\ \hline \hline \end{array}$	$\begin{array}{c} \beta_s^2 \\ \hline \hline \end{array}$	$\begin{array}{c} \beta_s / \sigma_B \\ \hline \hline \end{array}$	$\begin{array}{c} \alpha_s \beta_s / \sigma_A \sigma_B \\ \hline \hline \end{array}$	
$\begin{array}{c} \Sigma \div n \\ = M_B \end{array}$	$\Sigma = 0$	$\begin{array}{c} \Sigma \div n \\ = \sigma_B^2 \end{array}$	$\Sigma = 0$	$\begin{array}{c} \Sigma \div n \\ = r_{ab} \end{array}$	$\sigma_B = \dots$
$\begin{array}{c} C_s \\ \hline \hline \end{array}$	$\begin{array}{c} \gamma_s = M_C - C_s \\ \hline \hline \end{array}$	$\begin{array}{c} \gamma_s^2 \\ \hline \hline \end{array}$	$\begin{array}{c} \gamma_s / \sigma_C \\ \hline \hline \end{array}$	$\begin{array}{c} \alpha_s \gamma_s / \sigma_B \sigma_C \\ \hline \hline \end{array}$	$\begin{array}{c} \beta_s \gamma_s / \sigma_B \sigma_C \\ \hline \hline \end{array}$

Formula (15) is to be used for two sets, and formula (27) for three. This formula is a particular case of (26) for any number.

THE EFFECT OF CRYSTAL-SIZE ON LATTICE-DIMENSIONS

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ABSTRACT. The lattice constants of the lithium, sodium and potassium halides have been determined by the method of electron-diffraction, gold and graphite being used as reference standards. It has been found that crystal-size can and does exert an appreciable effect upon the lattice-dimensions.

§ 1. INTRODUCTION

THE use of zinc oxide as a reference material was advocated by Finch and Quarrell⁽¹⁾ in the determination of crystal-lattice constants by electron-diffraction. They took as constants those assigned by W. L. Bragg⁽²⁾ to zincite. Later, however, Finch and Wilman⁽³⁾ pointed out that more recent X-ray determinations of the constants of zincite and other specimens of specially pure zinc oxide differed, not only from Bragg's values, but also among themselves by as much as 1 per cent, and they therefore measured by electron-diffraction the lattice constants of zinc oxide prepared by the combustion of a zinc of forensic quality, gold leaf being used as reference standard. They obtained an axial ratio agreeing within the limits of experimental error with Bragg's value; their a and c values, however, exceeded not only Bragg's but also those due to all other X-ray investigators, by amounts which could certainly not be ascribed to errors in the measurement of diffraction-ring radii. It was shown furthermore that the discrepancy was not due either to thermal expansion or to charging-up effects, and the hope was then expressed that a redetermination might be carried out with X rays and condensed zinc-oxide smoke.

More recently it was suggested by one of us⁽⁴⁾ that the apparent discrepancy between the values of the lattice constants of zinc oxide as determined by diffraction of X rays and electrons respectively might be explained in terms of a theory first put forward in 1930 by Lennard-Jones⁽⁵⁾, according to whom the lattice-dimensions of crystals of homopolar compounds should increase with decreasing crystal size, whilst with ionic substances the reverse effect should occur.

X-ray experiments have been carried out by Lowry and Bozorth⁽⁶⁾, Randall and Rooksby⁽⁷⁾, Randall, Rooksby and Cooper⁽⁸⁾, and K. A. and U. Hofmann⁽⁹⁾, as a result of which it was suggested that in the case of certain glasses and carbons the lattice constants appeared to vary with the crystal-size in accordance with Lennard-Jones's theory. No certain conclusions could be drawn, however, because it was a question of detecting slight differences in the diameters of ill-defined haloes.

Owing to the far shorter wave-lengths available in electron-diffraction, it is quite easy to obtain a hundredfold increase in definition as compared with X rays when the overall dimensions of the diffracting crystals are less than about 100 Å.⁽¹⁷⁾ For this reason, and in order to put Lennard-Jones's theory to the test of experiment in the case of ionic compounds, determinations of the lattice constants of a series of alkali halides were carried out by the diffraction of high-speed electrons. Gold leaf was used and the results were checked by using the C—C spacing in the cleavage plane of graphite as a dimensional reference standard.

§ 2. EXPERIMENTAL

The camera was made in the Winnington Research Department of Messrs I.C.I. (Alkali) Ltd., from designs based on that of the instrument described elsewhere⁽¹⁰⁾. The cathode and camera sections were, however, separately evacuated by means of independent oil-vapour diffusion pumping systems, both backed by a high-speed rotary oil pump operating at about 0.01 mm. The diffusion pumps could be bye-passed by means of wide-bore Audco valves, an arrangement which permitted of opening the camera without cooling off the pumps and thus contributed greatly to an increased speed of operation.

Transmission patterns were recorded from specimens set up in one of the following ways: (i) Alkali halide was deposited on gold leaf, giving a composite diffraction pattern. (ii) Alkali halide or graphite was deposited on an amorphous collodion film supported on nickel gauze and gold supported on gold or nickel gauze. Double-shutter patterns were recorded in this case. (iii) The halide on collodion and that on gold were supported side by side and so close together on the same gauze that the electron beam, 0.1 mm. in diameter, passed through part of each specimen simultaneously and gave a composite alkali-halide and gold pattern.

The 24-ct. gold leaf supplied and guaranteed free from alloy by Messrs G. M. Whiley Ltd. was thinned in the usual manner by being floated on *N*/50 KCN solution and washed in several changes of distilled water. Samples of the leaves used in these experiments were double-shuttered with each other and also with specimens from the book originally used by Finch and Wilman in their determination of the lattice constants of zinc oxide. No difference could be detected in the corresponding lattice constants.

The lithium, sodium and potassium halides were the pure reagents supplied by Messrs Hopkins and Williams Ltd., mostly for analytical purposes. They were tested for those normally occurring impurities, other than waters of crystallization, the presence of which might be expected to affect the lattice constants. Thus, the sodium and potassium fluorides contained less than 0.05 and 0.2 per cent respectively of chlorides, and the sodium chloride less than 0.2 per cent of sulphate. The lithium and potassium salts gave the sodium flame test, but in no case was sodium present in sufficient amount for detection by precipitation as the dihydroxytartrate or zinc uranyl acetate. The potassium chloride was free from magnesium. Nitrates, bromides and iodides proved to be absent in the case of the

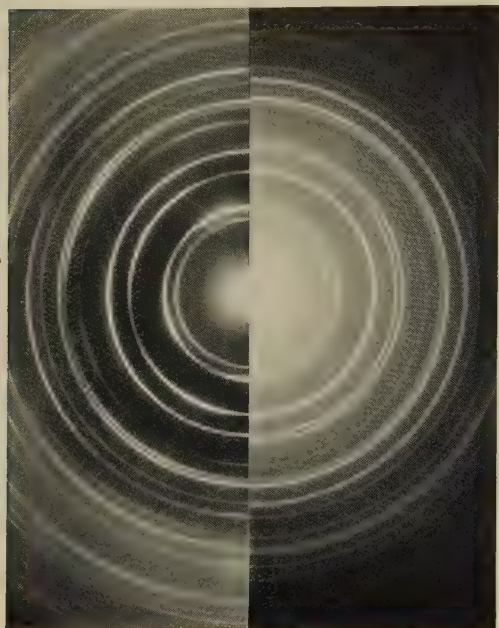


Figure 1. Gold (left) and lithium fluoride (right).

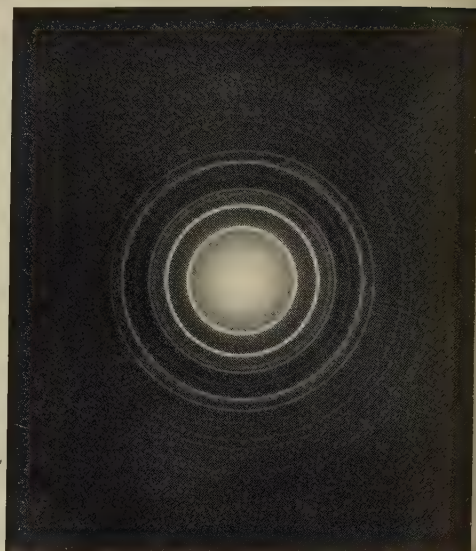


Figure 2. Potassium bromide superimposed on gold.

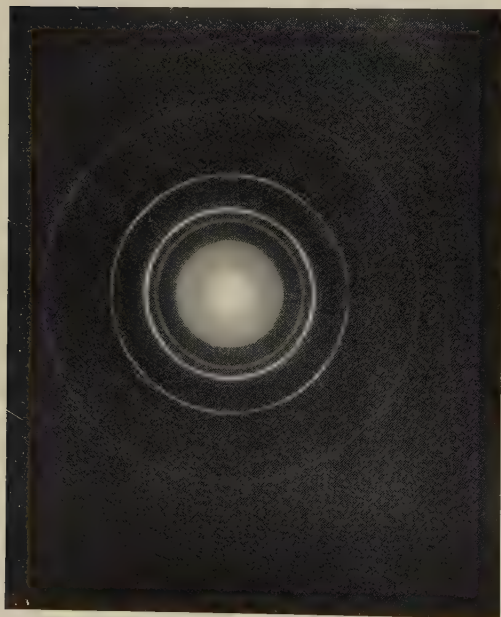


Figure 3. Sodium iodide superimposed on gold.

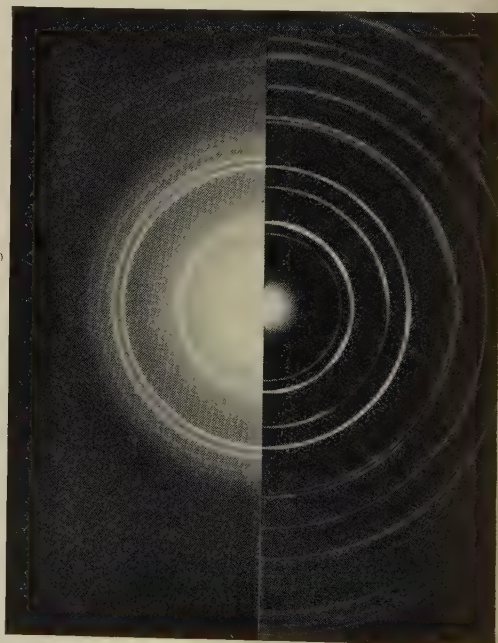


Figure 4. Graphite (left) and gold (right).

fluorides and chlorides. All the salts were completely soluble in water. The dried graphite contained 0.30 per cent of mineral ash.

The specimens were prepared by flashing in a vacuum of the order of 10^{-6} mm. from an appropriately coated tungsten filament, a procedure which removed any water of crystallization and would tend to reduce the amount of impurities if any were present. The graphite specimens were prepared by the evaporation of a dilute colloidal graphite solution (Aquadag) on a supporting collodion film.

§ 3. THE RESULTS

It will suffice for present purposes to reproduce four typical patterns: figure 1, lithium fluoride double-shuttered with gold; figure 2, potassium bromide superimposed on gold; figure 3, sodium iodide superimposed on gold; and figure 4, graphite double-shuttered with gold. It will be seen that they are such as to lend themselves well to accurate measurement. The results are set forth in the tables, and in order to illustrate the general method of computing the lattice constants, all necessary steps are given in table 1 in the case of the pattern for lithium fluoride double-shuttered with gold, figure 1.

Table 1. Plate F 118. LiF on collodion double-shuttered with gold

Ring-intensity	Ring-diameter (mm.)	Origin	log $2\lambda L$ from gold $a = 4.070 \text{ \AA.}$	log $2\lambda L$ interpolated	a for LiF (\AA.)
v.s.	22.245	Au 111	1.7183		
s.	22.485	LiF 111		1.7183	4.025
s.	25.705	Au 200	1.7183		
s.	25.95	LiF 200		1.7183	4.026
s.	36.335	Au 220	1.7184		
s.	36.72	LiF 220		1.7183	4.027
s.	42.605	Au 311	1.7187		
s.	43.03	LiF 311		1.7184	4.030
f.	44.53	Au 222	1.7186		
s.	44.95	LiF 222		1.7184	4.030
f.m.	51.41	Au 400	1.7183		
f.m.	51.985	LiF 400		1.7186	4.029
m.	55.99	Au 331	1.7184		
m.	56.595	LiF 331		1.7186	4.029
m.s.	57.45	Au 420	1.7188		
m.s.	58.125	LiF 420		1.7187	4.025
f.m.	62.985	Au 422	1.7188		
m.s.	63.65	LiF 422		1.7188	4.028
m.s.	66.82	Au 511	1.7187		
f.m.	67.52	LiF 511		1.7188	4.028
f.m.	72.74	Au 440	1.7188		
f.m.	73.545	LiF 440		1.7190	4.027
m.	76.05	Au 531	1.7190		
m.	76.945	LiF 531		1.7190	4.026
m.	77.20	Au 600	1.7189		
m.	78.07	LiF 600		1.7190	4.024
m.	81.34	Au 620	1.7189		
f.m.	82.26	LiF 620		1.7191	4.026
f.	84.44	Au 533	1.7194		
Mean from fourteen LiF rings					$4.027 + 0.003$ $- 0.003$

In column 1 the diffracted intensities are recorded as v.s. very strong, s. strong, m.s. medium strong, m. medium, f.m. faint to medium, and f. faint. The ring diameters were measured between opposite maxima by means of a Cambridge travelling microscope, so arranged as to project a hair-line image onto the photographic plate. $\log 2\lambda L$ in column 4 was calculated from the equation

$$2\lambda L = \frac{4.070D}{\sqrt{(h^2 + k^2 + l^2)}} \quad \dots\dots(1),$$

where λ is the wave-length in angstroms, L is the camera-length in millimetres, D is the diameter of the ring in millimetres, and h , k and l are the Laue indices defining the diffraction.

The values of $\log 2\lambda L$ in column 5 were obtained by interpolation from those in column 4, whence a for lithium fluoride in column 6 is given by

$$a = \frac{2\lambda L \sqrt{(h^2 + k^2 + l^2)}}{D}.$$

The advantage of this apparently roundabout procedure is that any deviation from Bragg's law such as might occur, for example, in the event of the refraction of electrons entering and leaving the same crystal-face, would immediately be made evident. The slight increase in the values of $\log 2\lambda L$ with increasing ring-diameter is due to the fact that equation (1) assumes a spherical recording-field, with a radius of about 48 cm., about the effective specimen, whereas the photographic plate is in fact flat. The complete final results are given in table 2.

In the specification of the crystal-size, "small", "medium" and "large" mean about 40, 60 and 100 Å. or more, respectively, but the large crystals were probably submicroscopic as judged by ring-homogeneity. Some specimens yielded sharp continuous rings with superimposed spots; they consisted of large and very large crystals. Since the measurements were made to the homogeneous portions of the rings, however, the effective crystal-size in such cases was large, and has been entered as such in column 6, table 2.

The overall error in the graphite results is, as in the case of all double-shutter patterns, almost certainly due to change in camera-length by amounts of the order of 1 mm. or less, such as is sometimes difficult to avoid on translation of the specimen-carrier between exposures, when the second specimen-half is being brought into the electron beam.

In table 3 are given the means of the lattice constants as set forth in table 2, together with the corresponding X-ray values and the differences between the lattice constants as found by electron-diffraction and X-ray-diffraction respectively. Unless the contrary is stated, the X-ray values are those due to Ewald and Hermann's critical selection in their 1931 supplement to the *Strukturbericht* of the *Zeitschrift für Krystallographie*. As far as we have been able to ascertain, all the X-ray values, including that of gold, are referred to that of sodium chloride ($a = 5.6280$ Å.) either directly or through secondary standards. Finch and Wilman's⁽³⁾ electron-diffraction and Bunn's⁽¹²⁾ recent X-ray values of the lattice constants of similar samples of coagulated zinc-oxide smoke have also been included in table 3.

Table 2

Substance	Plate No.	Type of pattern	Number of rings other than gold	Mean value of a (Å.)	Crystal-size
LiF	F 117	Double-shutter	16	4.028 $\begin{smallmatrix} +0.004 \\ -0.004 \end{smallmatrix}$	Medium
LiF	F 118	Double-shutter	14	4.027 $\begin{smallmatrix} +0.003 \\ -0.003 \end{smallmatrix}$	Medium
LiCl	F 72	Superimposed	7	5.136 $\begin{smallmatrix} +0.003 \\ -0.003 \end{smallmatrix}$	Large
LiBr	F 171	Double-shutter	15	5.500 $\begin{smallmatrix} +0.009 \\ -0.011 \end{smallmatrix}$	Large
LiBr	F 173	Double-shutter	16	5.490 $\begin{smallmatrix} +0.013 \\ -0.006 \end{smallmatrix}$	Large
LiI	F 176	Adjoining specimens	15	6.019 $\begin{smallmatrix} +0.012 \\ -0.010 \end{smallmatrix}$	Medium
NaF	F 53	Superimposed	4	4.641 $\begin{smallmatrix} +0.002 \\ -0.005 \end{smallmatrix}$	Small
NaF	F 170	Double-shutter	7	4.641 $\begin{smallmatrix} +0.009 \\ -0.006 \end{smallmatrix}$	Small
NaCl	F 36	Superimposed	6	5.672 $\begin{smallmatrix} +0.010 \\ -0.013 \end{smallmatrix}$	Medium
NaCl	F 34	Superimposed	9	5.666 $\begin{smallmatrix} +0.010 \\ -0.014 \end{smallmatrix}$	Medium
NaBr	F 52	Superimposed	6	5.966 $\begin{smallmatrix} +0.004 \\ -0.006 \end{smallmatrix}$	Medium
NaBr	F 51	Superimposed	9	5.959 $\begin{smallmatrix} +0.014^* \\ -0.015 \end{smallmatrix}$	Large
NaI	F 69	Superimposed	7	6.468 $\begin{smallmatrix} +0.011 \\ -0.008 \end{smallmatrix}$	Large
NaI	F 68	Superimposed	10	6.469 $\begin{smallmatrix} +0.005 \\ -0.006 \end{smallmatrix}$	Large
KF	B 719	Superimposed	5	5.356 $\begin{smallmatrix} +0.012 \\ -0.013 \end{smallmatrix}$	Small
KCl	F 4	Superimposed	6	6.321 $\begin{smallmatrix} +0.010 \\ -0.007 \end{smallmatrix}$	Medium
KCl	F 6	Superimposed	5	6.317 $\begin{smallmatrix} +0.007 \\ -0.006 \end{smallmatrix}$	Medium
KBr	F 11	Superimposed	11	6.631 $\begin{smallmatrix} +0.008 \\ -0.010 \end{smallmatrix}$	Large
KBr	F 12	Superimposed	11	6.630 $\begin{smallmatrix} +0.004 \\ -0.005 \end{smallmatrix}$	Large
KI	F 17	Superimposed	7	7.078 $\begin{smallmatrix} +0.014 \\ -0.010 \end{smallmatrix}$	Medium
Graphite	F 90	Double-shutter	3	2.462 $\begin{smallmatrix} +0.001 \\ -0.001 \end{smallmatrix}$	Large
Graphite	F 96	Double-shutter	3	2.460 $\begin{smallmatrix} +0.001 \\ -0.001 \end{smallmatrix}$	Large
Graphite	F 99	Double-shutter	3	2.449 $\begin{smallmatrix} +0.001 \\ -0.003 \end{smallmatrix}$	Large
Graphite	F 102	Double-shutter	3	2.459 $\begin{smallmatrix} +0.002 \\ -0.002 \end{smallmatrix}$	Large
Graphite	F 104	Double-shutter	4	2.453 $\begin{smallmatrix} +0.000 \\ -0.000 \end{smallmatrix}$	Large
Graphite	F 107	Double-shutter	4	2.466 $\begin{smallmatrix} +0.001 \\ -0.002 \end{smallmatrix}$	Large
Graphite	F 109	Double-shutter	4	2.456 $\begin{smallmatrix} +0.002 \\ -0.004 \end{smallmatrix}$	Large
Graphite	F 113	Double-shutter	4	2.455 $\begin{smallmatrix} +0.001 \\ -0.000 \end{smallmatrix}$	Large
Graphite	F 114	Double-shutter	3	2.460 $\begin{smallmatrix} +0.003 \\ -0.003 \end{smallmatrix}$	Large

* The width of the error in this case was due in the main to the faintness of the sodium wide rings in this one pattern.

§ 4. DISCUSSION OF RESULTS

From the results set forth in table 3 it will be seen that the values of the lattice constants of lithium fluoride, chloride and bromide, of sodium bromide and iodide, and of potassium fluoride as determined by electron-diffraction agree within the experimental error with those previously found with X rays though, except in the

Table 3

Substance	Type of pattern	Crystal-size	a (Å.) referred by electron-diffraction to the value $4\cdot070$ of a_{Au}	a (Å.) by X rays	Difference (Å.)
LiF	Double-shutter	Medium	$4\cdot027 \pm 0\cdot005$	$4\cdot020 \pm 0\cdot002$	$+0\cdot007$
LiCl	Superimposed	Large	$5\cdot136 \pm 0\cdot003$	$5\cdot143 \pm 0\cdot006$	$-0\cdot007$
LiBr	Double-shutter	Large	$5\cdot495 \pm 0\cdot008$	$5\cdot489 \pm 0\cdot006^{(11)}$	$+0\cdot006$
LiI	Adjoining specimens	Medium	$6\cdot019 \pm 0\cdot005$	$6\cdot000 \pm 0\cdot007$	$+0\cdot019$
NaF	Superimposed	Small	$4\cdot641 \pm 0\cdot004$	$4\cdot619 \pm 0\cdot002$	$+0\cdot022$
	Double-shutter				
NaCl	Superimposed	Medium	$5\cdot669 \pm 0\cdot005$	$5\cdot6280$	$+0\cdot041$
NaBr	Superimposed	Large	$5\cdot963 \pm 0\cdot005$	$5\cdot962 \pm 0\cdot002$	$+0\cdot001$
NaI	Superimposed	Large	$6\cdot469 \pm 0\cdot005$	$6\cdot462 \pm 0\cdot006$	$+0\cdot007$
KF	Superimposed	Small	$5\cdot356 \pm 0\cdot010$	$5\cdot36$?
KCl	Superimposed	Medium	$6\cdot319 \pm 0\cdot005$	$6\cdot277 \pm 0\cdot002$	$+0\cdot042$
KBr	Superimposed	Large	$6\cdot630 \pm 0\cdot004$	$6\cdot586 \pm 0\cdot002$	$+0\cdot044$
KI	Superimposed	Medium	$7\cdot078 \pm 0\cdot008$	$7\cdot052 \pm 0\cdot003$	$+0\cdot026$
Graphite	Double-shutter	Large	$2\cdot458 \pm 0\cdot005$	$2\cdot45 \pm 0\cdot03^{(19)}$?
ZnO	Superimposed	Large	$a = 3\cdot258 \pm 0\cdot005$ $c = 5\cdot239 \pm 0\cdot005$	$a = 3\cdot2426$ $c = 5\cdot1948$	$+0\cdot015$ $+0\cdot044$

case of lithium chloride, there is a marked tendency for the electron-diffraction values slightly to exceed those due to X rays. On the other hand, lithium iodide, sodium fluoride and chloride, and potassium chloride, bromide and iodide are like zinc oxide, in giving by electron-diffraction values of the lattice constants higher than those obtained with X rays. The differences in most cases greatly exceed the combined experimental errors due to both methods. In what follows it is our object to elucidate the origin of this discrepancy.

The gold-leaf reference standards employed in these experiments were withdrawn from the same book. The lithium fluoride and bromide, the sodium fluoride and two graphites (F 113 and 114) were compared with the same gold specimen. Of the remaining fourteen gold specimens, seven were compared by the double-shutter method with graphite specimens prepared from the same batch. As is shown in table 2, the individual values of a for graphite agree satisfactorily. In all the graphite specimens the crystals were oriented with the slip planes parallel, or nearly so, to the collodion substrate. The approximate size and shape of colloidal graphite particles have been determined by electron-diffraction by Jenkins⁽¹³⁾ and more recently by Finch, Quarrell and Wilman⁽¹⁰⁾. The fact that beautifully clear and

sharp ring patterns can be obtained by transmission through such graphite films when they are supported on collodion shows that the average particle-size is about 200 Å. or less along the c axis, but greater in directions normal to that axis; whilst reflection experiments suggest that the particle extent in the planes of the carbon hexagons exceeds 600 Å. Thus, bearing in mind the weak attraction between the neighbouring hexagon planes and the very strong C—C bindings within the hexagons, one may reasonably suppose that for the range of particle-size employed in these experiments the value of a for graphite is virtually independent of the crystal-size. From the results recorded in tables 2 and 3 we may therefore conclude that, within the present limits of accuracy, the lattice-dimensions of the gold leaf serving as reference standards in these experiments were constant. It should be noted, however, that, owing to the limited accuracy with which a for graphite has been determined by X rays, it cannot be assumed that our results prove that the lattice constant obtained for the gold was equal to the X-ray value.

Impurities in the halides examined might affect the values of the lattice constant. Davighurst, Mack and Blake⁽¹⁴⁾ were, however, unable to detect any such effect in the case of ammonium and caesium chlorides containing less than 3 per cent of potassium, caesium or rubidium chlorides, and Vergard and Hauge⁽¹⁵⁾ have shown that the lattice-dimensions of mixed crystals of potassium chloride and bromide vary linearly with composition between the appropriate limits. Thus it seems clear that, in order to give rise to differences of the order of magnitude observed in some of our experiments, gross amounts of impurities would have had to be present in the specimens, whereas analysis showed the materials to be free from all but negligible impurity-contents. Furthermore, in the case of the potassium halides, the tendency of any chemically likely impurity would have been to reduce, but not to increase, the values of the lattice constants.

The halide specimens were supported on either gold or amorphous collodion substrates. Finch and Quarrell⁽²⁰⁾ have shown that the substrate can exert a profound effect upon the structure, and hence upon the lattice constants of a deposited film. It cannot be supposed, however, that any such pulling into step by the gold substrate of the constituent atoms of the halides occurred in our experiments, because one of the two sodium-fluoride specimens was superimposed on gold and the other on amorphous collodion; nevertheless, both gave results which are in good agreement with each other, though they are higher by 0.4 per cent than the corresponding X-ray value. Furthermore, whilst lithium chloride, and sodium iodide and bromide, all superimposed on gold, gave normal values, similarly mounted specimens of sodium fluoride and chloride, and of potassium chloride, bromide and iodide yielded high electron-diffraction values, in some cases exceeding the corresponding X-ray constant by as much as 0.7 per cent. Finally, although the lithium chloride was deposited on gold but the other lithium halides on collodion, only the iodide gave a high value. Thus these facts seem effectively to negative any explanation of the differences between the electron and X-ray results as being due to a substrate effect.

Thomson⁽¹⁶⁾ has considered the possibility of electrons entering and leaving

through the same crystal faces in polycrystalline specimens. If the crystals were too thick to transmit, this would result in a decrease in ring diameters, relatively large in the case of the inner rings, but decreasing rapidly with increasing angle of refraction, and becoming negligible in the case of the outer rings. As may be seen from table 1, which may be taken as representative of our measurements, we have, however, in no case been able to detect any systematic variation either in $\log 2\lambda L$ or in the lattice constants deduced from the ring diameters on proceeding outwards from the central spot, other than that due to the flatness of the recording field, an effect which is at least ten times smaller than the refraction effect now under consideration. Again, irrespective of whether the rings are sharp, as in the case of large crystals, or broadened, as in the case of small crystals, the diameters measured between opposite maxima always lead to lattice-constant values which are independent of the ring-diameters. Furthermore, we would expect any pronounced refraction effect to be accompanied by much intense background (zero order) within the innermost ring; apart from the usual halation in the immediate vicinity of the spot, however, the patterns are singularly free from such background. Thus these facts and considerations seem to preclude any possibility of accounting for the abnormally high electron-diffraction values of the lattice constant in terms of refraction by exposed faces.

To sum up. The discrepancies between the X-ray and electron-diffraction values of the lattice constants of certain of the alkali halides enumerated in table 3 cannot reasonably be attributed to (i) a variation in the lattice constant of the gold reference standards, or to (ii) impurities in the halides examined, or to (iii) lattice-distortion through a substrate influence, or to (iv) the coming into play of refractive index effects.

Excessive tolerance in the critical angle of incidence, exceeding, say, 5° , such as has been shown by Finch, Quarrell and Wilman⁽¹⁰⁾ to occur with crystals of extreme thinness in the direction of the beam, would lead not only to a broadening of the rings, but also to an increase in diameter as measured between maxima. Such an effect was not observed and would in any case have led to low electron-diffraction values for the lattice constants.

It is possible from certain features of the patterns to form a very rough estimate of the average size of the halide crystals in the specimens examined. The absence of effects due to excessive tolerance in the angle of incidence suggests a lower limit of particle thickness of roughly 50 Å. in the direction of the beam. The freedom from background, particularly inside the innermost rings, places the upper limit of particle thickness as well within 150 Å. From the ring definition it can be calculated⁽¹⁷⁾ that the mean overall crystal dimensions in directions normal to the beam varied according to the specimen from about 40 Å. to 100 Å. or more, and very much more in the case of those crystals which gave rise to spots. In those patterns where spots were obtained, however, they were always superimposed on continuous rings, and since the rings but not the spots served for measurement, the effective crystal-size was of the same order as for those specimens that yielded patterns with perfectly sharp rings without spots. No possible diffraction was found to be missing in any

the halide patterns. This fact suggests that there was little if any orientation of the crystals. Hence, in view of the cubic symmetry and the clarity of the patterns, it seems reasonable to suppose that the upper limit in the dimensions of the effectively diffracting crystals was less than 150 Å. in every direction. Whytelaw-Gray and others⁽¹⁸⁾ found that zinc-oxide smoke on coagulation formed chains of beads about 200 Å. in diameter strung together by links, presumably hairs, so fine as to be invisible through the microscope. The definition and clarity of Finch and Wilman's zinc-oxide patterns are such that the overall dimensions of the effectively diffracting crystals in their specimens must have been not less than 100 Å. and not more than 50 Å. in the direction of the beam. Thus it seems clear that the zinc-oxide electron-diffraction patterns were due to the invisible hairs, because the size of the beads is such as virtually to preclude their contributing to the diffraction pattern. Conversely, in the case of a similar coagulated zinc-oxide smoke examined with X rays the pattern would be almost entirely produced by the microscopic beads, whose mass must greatly outweigh that of the filamentary links which, with an average diameter of the order of 100 Å., would with X rays in any case give rise only to ill-defined haloes. Thus it appears certain that although their zinc-oxide specimens had been prepared in a similar manner and from the same batch of zinc of forensic quality, Finch and Wilman in effect obtained their patterns with crystals of submicroscopic dimensions, whereas those which were effective in producing Bunn's very sharp X-ray powder patterns were at least ten times larger. Similarly, in the case of the halides there is little room for doubt that there existed a similar or even much greater difference in size between the crystals diffracting electrons and X rays respectively.

In the light of these facts and considerations, and in the absence of any other reasonable explanation, it seems to us that the observed differences in the values of the lattice constants of zinc oxide and of certain alkali halides obtained by electron-diffraction and X-ray diffraction respectively are due to a real variation in the lattice-dimensions with crystal-size. In general, the effect is such that the lattice constants appear to be larger for the submicroscopic electron-diffracting crystals than for those of a size effective in yielding sharp X-ray diffractions. Owing to the uncertainty of the X-ray value of a for graphite, however, it is still possible, though perhaps somewhat unlikely, that the value of a for gold having the crystal-size employed by us differs appreciably from the accepted X-ray value of 4.070 Å. However this may be, the results set forth above enable the conclusion to be drawn that crystal-size can and sometimes does exert an appreciable effect upon the lattice-dimensions of ionic crystals.

§ 5. ACKNOWLEDGMENTS

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A DETERMINATION OF THE SPECIFIC HEATS OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE

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ABSTRACT. The specific heats of aqueous solutions of potassium chloride have been measured between 15° C. and 45° C., over a range of concentration $\frac{1}{10}$ *N* to 2.5 *N*. The method of measurement employed was that devised by Ferguson and Miller, slightly modified for use with conducting liquids.

§ 1. INTRODUCTION

IN continuation of an investigation of some of the physical properties of solutions of strong electrolytes carried out in this laboratory during the past few years^(1,2,3,4), it was considered desirable to study the variation of their specific heats with temperature and concentration. There is quite an extensive literature on the subject, the most valuable work being that of Randall and Rossini^(5,6) and of Richards and his collaborators⁽⁷⁾. Much of this, however, did not relate to the direct measurement of specific heat, which was calculated from the heat of dilution. Further, most of the work was carried out at 25° C., and it seemed therefore desirable that observations should be made over a much wider range of temperature.

§ 2. METHOD

The method employed was that described by Ferguson and Miller⁽⁸⁾. Their measurements showed that it was capable of quite high accuracy. Since the publication of their first paper they have made an extensive series of measurements on a number of organic liquids.* They have used a calorimeter of about half the capacity of the original, i.e., about 500 cm.³, while the voltages were measured on a more accurate type of potentiometer reading to 1 μ V. It was this apparatus that was used in the present work.

The thermometer which recorded the temperature of the calorimeter and its contents was a first-grade instrument supplied by B. Black and Son, graduated in tenths from -10° to 105° C. With the aid of a low-power microscope readings could be taken to 0.01°. This thermometer was calibrated at the National Physical Laboratory against the standard thermometers, at intervals of ten degrees from 0° to 100°, the limit of accuracy of the test being $\pm 0.02^\circ$ C. The calibration was for partial immersion. It is possible to read a temperature on a descending scale, in

* Unpublished.

spite of this being usually regarded as a difficult operation as is evident from the smoothness of the cooling curve.

$E, R,$
 θ It will be recalled that electrical power is supplied to the copper calorimeter and its contents to hold the temperature stationary $5^\circ, 10^\circ \dots$ above that of the surroundings. If E^2/R watts* are supplied and the temperature excess over the surroundings is θ° we have

$$-\frac{d\theta}{dt} = -(MS + W) \frac{d\theta}{dt} = \frac{E^2}{JR} \quad \dots\dots(1),$$

M, S
 W
 t where M is the mass of the liquid in the calorimeter, S its specific heat at a temperature θ° above that of the surroundings, W the water equivalent of the calorimeter and its accessories, and $-d\theta/dt$ the rate of loss of heat from the calorimeter and its contents at temperature-excess θ° .

It is found empirically that

K

$$-\frac{d\theta}{dt} = K\theta^{\frac{5}{4}} \quad \dots\dots(2).$$

The validity of this equation may be established as follows. Integrating (2), we have

$$\theta^{-\frac{1}{4}} - \theta_0^{-\frac{1}{4}} = \frac{1}{4}Kt \quad \dots\dots(3).$$

A series of values of θ and t are obtained from a cooling experiment, so that if we plot $\theta^{-\frac{1}{4}}$ against t we should obtain a straight line, the slope of which determines K , if equation (2) holds. K is a constant for a given solution and calorimeter, but varies slightly from solution to solution. It is separately determined for each run. We thus obtain the equation

$$(MS + W) K\theta^{\frac{5}{4}} = E^2/RJ \quad \dots\dots(4),$$

for the determination of S .

The water equivalent is determined by making a complete run with water as the experimental liquid, and substituting values taken from the International Critical Tables for the specific heat of water. This gives the relation

$$W_T = W_0 (1 + 0.0005009 T)$$

T for the variation of the water equivalent with temperature, where T is in degrees centigrade.

§ 3. MODIFICATION OF CALORIMETER FOR CONDUCTING LIQUIDS

It was obvious that for conducting liquids such as electrolytes it would be necessary to insulate the heating-coil and leads. A very thin coat of cellulose lacquer was applied to the coil, leads, and inner wall of the calorimeter, but a run with a normal solution of potassium chloride soon revealed the necessity for better insulation and for keeping the solution from contact with copper. The calorimeter was therefore chromium-plated.

* International watts, the appropriate value of J being 4.1845. If we follow the recommendation in the S.U.N. report of the International Conference on Physics, that the unit of heat when measured in units of energy be the force defined as 10^7 ergs, the value of J is 4.186. This change involves an alteration of about 0.05 per cent in the values of specific heats given in this paper.

After a number of methods of insulating the coil had been tried, that finally used was to apply a thin coat of Bakelite varnish which was baked on.

Apart from these minor though necessary alterations, Ferguson and Miller's procedure was adhered to throughout.

§ 4. RESULTS

All measurements were made with accurately prepared solutions, the water being obtained from a conductivity still. The salts were of analytical-reagent standard. As soon as the solution had been prepared it was put into the calorimeter and a complete run was carried out. The solutions were never allowed to stand in the calorimeter for more than two days. As a rule the whole experiment was completed within six or seven hours.

The results of the measurements on solutions of concentrations ranging from $\frac{1}{10}N$ to $2.5N$ are collected in tables 1 and 2. In this work a normal solution is defined as one containing 1 gram-molecule (74.553 g.) of potassium chloride in 1000 g. of water. When the results are plotted it is found that the temperature coefficient decreases with concentration, until with a $\frac{1}{2}N$ solution it is zero within the limits of experimental error. Below this concentration an approximately parabolic curve is obtained when specific heat is plotted against temperature, as in the case of water.*

Table 1

(a) Heating experiments. Normal solution of potassium chloride.
Mass of liquid, 495.45 g.

E (V.)	Temperature of surroundings	Temperature of calorimeter	Temperature excess	Water equivalent W	Specific heat
0.1841 ₅	13.34	15.21	1.87	66.47	0.911 ₄
0.4111 ₉	13.34	18.96	5.62	66.64	0.912 ₀
0.5704 ₀	13.35	24.75	11.40	66.83	0.912 ₅
0.7180 ₉	13.36	29.82	16.46	67.08	0.913 ₆
0.9118 ₂	13.36	37.44	24.08	67.38	0.915 ₁
1.0136 ₈	13.37	41.87	28.50	67.48	0.916 ₃

(b) Cooling experiments. $K = 0.06972 \times 10^{-3}$.

Temperature of calorimeter	Temperature of surroundings	Time t (sec.)	Temperature of calorimeter	Temperature of surroundings	Time t (sec.)
31.32	13.34	0	26.33	13.36	2400
30.59	13.35	300	25.32	13.35	3000
29.88	13.36	600	24.46	13.35	3600
28.59	13.37	1200	23.62	13.35	4200
27.29	13.37	1860	18.50	13.33	10200

While the accuracy of the work is quite reasonably high, it is not however sufficiently great for us to calculate some of the associated thermodynamic functions

* Work on the specific heat of water is now in progress.

Table 2. Potassium chloride

2.5 N	$T(^{\circ}\text{C.})$ S	15.61 0.813 ₈	19.14 0.814 ₇	23.32 0.816 ₉	25.79 0.817 ₇	31.66 0.820 ₁	37.20 0.822 ₃	40.53 0.824 ₂	
2 N	$T(^{\circ}\text{C.})$ S	14.72 0.839 ₀	17.96 0.840 ₅	21.13 0.842 ₂	26.22 0.843 ₇	30.47 0.845 ₂	33.81 0.846 ₀	36.65 0.847 ₁	40.04 0.849 ₀
1.5 N	$T(^{\circ}\text{C.})$ S	14.94 0.872 ₂	18.95 0.873 ₅	24.96 0.875 ₀	28.57 0.875 ₅	32.90 0.876 ₅	38.24 0.877 ₃	45.06 0.879 ₄	
0.75 N	$T(^{\circ}\text{C.})$ S	22.61 0.931 ₈	28.97 0.932 ₄	34.48 0.933 ₃	40.85 0.934 ₁	44.41 0.934 ₂	50.64 0.935 ₀		
0.5 N	$T(^{\circ}\text{C.})$ S	16.11 0.955 ₈	20.95 0.955 ₂	26.76 0.955 ₆	31.48 0.955 ₈	33.90 0.955 ₄	38.42 0.955 ₇	42.78 0.955 ₈	
0.5 N	$T(^{\circ}\text{C.})$ S	16.27 0.956 ₀	22.25 0.955 ₇	29.81 0.955 ₈	36.34 0.955 ₄	42.63 0.956 ₁			
0.1 N	$T(^{\circ}\text{C.})$ S	16.37 0.988 ₅	19.30 0.987 ₁	23.86 0.987 ₂	29.11 0.987 ₁	33.73 0.987 ₅	38.82 0.987 ₉	43.15 0.988 ₂	

such as the apparent partial molal heat-capacity of the electrolyte. It is not therefore possible to test the agreement of the present data with the Debye theory which predicts that the partial molal heat-capacity should vary linearly with the square root of the concentration. For such calculations to be made an accuracy of about 1 part in 10,000 is required.

Randall and Rossini have derived the expression

$$C_p = 2.14 (\Sigma \nu_1 z_1^2)^{\frac{3}{2}} m^{\frac{1}{2}} + C_{p_0} \quad \dots\dots(5),$$

where C_p is the partial molal heat-capacity, and m the molarity, while $\Sigma \nu_1 z_1^2$ is the valence factor. C_{p_0} is the value of the partial molal heat-capacity at infinite dilution. Later work may permit of a strict test of the above relation over a temperature-range, its validity at 25° C. having been proved for a number of electrolytes of different types⁽⁵⁾.

Theory does not predict any simple relation between specific heat and concentration, nor do the experimental data suggest one. The equation connecting the specific heat and the partial molal heat,

$$C_p = S \left[\frac{1000}{m} + M \right] - \frac{1000}{m} \quad \dots\dots(6),$$

taken in conjunction with the theoretical relationship between C_p and the concentration, equation (5), shows immediately that the specific heat is a complex function of the molarity.

§ 5. CONCLUSIONS

The present preliminary note is designed to show the possibility of determining the specific heats of solutions of electrolytes and their variation with temperature over a relatively wide range of temperature with a fairly high degree of accuracy. In

In a later communication it is hoped to extend these results in range and in accuracy, and to discuss their theoretical bearing.

§ 6. ACKNOWLEDGMENTS

I have much pleasure in expressing my thanks to Prof. H. R. Robinson, F.R.S., and to Dr Allan Ferguson for the facilities they have placed at my disposal and for their advice and encouragement. I am indebted to the Department of Scientific and Industrial Research for a grant which made it possible to carry out this work.

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THE CONDUCTIVITY OF AN ORIFICE IN THE END OF A PIPE

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ABSTRACT. The conductivity of an orifice in an infinite plane of negligible thickness was shown by the late Lord Rayleigh to be equal to its diameter d . The writer extended this formula to include the conductivity when one side of the plane is enclosed by a concentric pipe of diameter D , which thus forms a cylindrical resonator fitted with an infinite plane at the mouth, and deduced the expression $d \cdot 2^{d/D}$ for the conductivity. This expression is supported by experimental results quoted in the present paper.

k, r **T**HE resistance experienced by an alternating current of fluid entering a semi-infinite atmosphere of the fluid from an orifice in an infinite plane is equal to ⁽¹⁾ $1/4kr$, where k stands for the conductance of the medium and r for the radius of the orifice.* This formula also holds if the current enters the orifice from the semi-infinite atmosphere, hence the resistance encountered by the alternating current in passing into a semi-infinite atmosphere from a similar atmosphere through an extremely thin orifice is given by

$$1/2kr.$$

By putting k equal to 1, we make the conductivity of the orifice $2r$, which is equal to the diameter and is the well-known value for the acoustical conductivity for such an orifice ⁽²⁾.

d If, however, the efflux takes place through a pipe of radius r terminating in an infinite flange, the resistance *due to the orifice* is $1/4kr$, and therefore the conductivity of the latter is $2d$, where d is the diameter.

If the pipe is of larger radius than the orifice, the conductivity will lie between d and $2d$. The writer has shown ⁽³⁾ that the expression

$$C = d \cdot 2^{d/D},$$

C closely represents the conductivity C of an orifice of diameter d in the end of a pipe of diameter D , fitted with an infinite flange.

N. W. Robinson ⁽⁴⁾ used this formula for calculating the conductivities of orifices

* The resistance $1/4kr$ is only true for direct current, but is very near the truth for a.c. of low frequency. Rayleigh made this assumption in developing the theory of resonators, see *Sound*, p. 170.

For comparison with results obtained by him experimentally and shown in the table.

Table

Diameter d of orifice (cm.)		4.0	3.5	3.0	2.5	2.0	1.5	1.0
Mean of conductivities at 875 to 1120 c./sec.	Experimental	8.38	6.67	5.30	4.05	3.04	2.08	1.28
	Calculated	7.02	5.73	4.58	3.56	2.65	1.86	1.15
Reduced conductivity at 875 c./sec.		6.9	5.72*	4.62	3.54	2.49	1.79	1.10

* The actual figure given for the 3.5-cm. orifice is 5.53, but, from the run of the table, it appears that this should be 5.23. This reduces, for a thin plate, to 5.72, the value given above.

Unfortunately, in these experiments it was necessary for the diameter of the pipe, which was about 5 cm., to be small in comparison with the wave-length of the sound used. Robinson used frequencies of 875, 912, 1000 and 1120 c./sec., and his results show a considerable increase of conductivity with frequency in practically every case.

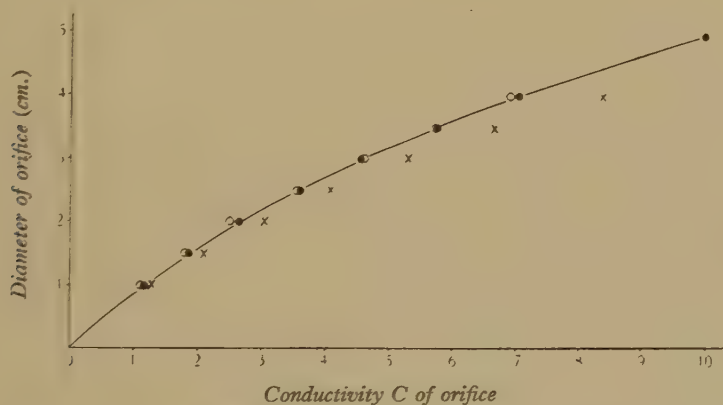


Figure 1. ● Formula, $C = d \cdot 2^d / D$; × Robinson, experimental; ○ Robinson, reduced results.

The experimental results given above are the mean values for the four frequencies, whereas the values for the lowest frequency, quoted in table 3 of Robinson's paper⁽⁴⁾ have, when reduced so as to be applicable to a thin plate, the values shown in the last line of the accompanying table.

It will be seen from the graph that these are practically the same as the calculated values, and therefore confirm the formula.

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THE ABSOLUTE MEASUREMENT OF THE VISCOSITY OF LIQUID TIN

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ABSTRACT. By the capillary-flow method the viscosity of liquid tin has been measured over a range of temperature just above the melting-point. The kinetic-energy correction has been determined independently by the use of Knibbs's graphical method. The viscosity values are in good agreement with the measurements of Stott, and confirm the general accuracy of the work of Sauerwald and Töpler. The temperature variation of the viscosity and the value at the freezing-point can be adequately represented by Andrade's theory of the viscosity of liquids.

§ 1. INTRODUCTION

IN the course of a series of investigations on the temperature variation of certain properties of the metal tin it was realized that more reliable data were needed for the viscosity of the liquid metal at temperatures near the melting-point. This paper gives a brief account of detailed measurements of the viscosity of liquid tin over the range of temperature 235°C . to 330°C .

The viscosity of liquid tin and other metals has been measured by Arpi⁽¹⁾, Plüss⁽²⁾, and Sauerwald and Töpler⁽³⁾, using the capillary-flow method, and by Fawsitt⁽⁴⁾, using the oscillating disc method. The results obtained differ considerably; the measurements of Sauerwald and Töpler appear to be the most accurate of those mentioned.

Recently measurements on the viscosity of liquid tin have been made by Stott⁽⁵⁾ by the use of an oscillating disc. By using the results of Sauerwald and Töpler for calibration purposes, Stott has extended the range of temperature for which the viscosity may be taken as fairly well established, but has pointed out the desirability of checking the measurements of Sauerwald and Töpler.

§ 2. METHOD

After a close examination of the available methods, the capillary-flow method was chosen since it appeared most capable of providing absolute values; all oscillatory methods were rejected owing to the theoretical uncertainties which they involve.

t
 V The capillary-flow method is that in which the time t taken by a known volume V of the liquid to flow through a vertical capillary tube under a known pressure-

difference P is measured. If r is the radius of the capillary and l its length, the viscosity η is given by the simple Poiseuille relation P, r, l
 η

$$\eta = \frac{\pi P r^4}{8 V l},$$

all corrections being ignored.

§ 3. THEORETICAL CORRECTIONS

The kinetic-energy correction. The simple Poiseuille law is derived on the assumption that all the energy supplied during flow is used in overcoming viscous resistance within the fluid. If moderate or high speeds are used, a correction for the gain in kinetic energy is necessary. The final formula for the viscosity with this correction was first given by Hagenbach as

$$\eta = \frac{\pi P r^4}{8 V l} - \frac{m V \rho}{8 \pi l t} \quad \dots\dots(1),$$

where m is a constant and ρ is the density of the liquid. m, ρ

Various theoretical values of the constant m , ranging from 1.00 to 1.12, have been proposed from time to time. In practice, however, there is evidence that m is not strictly the same for all tubes and that it may even vary slightly for a single tube. The kinetic-energy correction is of especial importance in the case of liquid metals, since the density is a multiplying factor in the correction term.

Knibbs's method⁽⁶⁾. Fortunately Knibbs's experimental procedure provides a valuable method of estimating whether or not m is constant for a particular tube, and for independently estimating its magnitude. Equation (2) can be re-written

$$Pt = a + \frac{b}{t},$$

where a, b

$$a = \frac{8 \eta V l}{r^4 \pi} \quad \text{and} \quad b = \frac{m \rho V^2}{\pi^2 r^4}.$$

If Pt is plotted against $1/t$ for a given tube and liquid, we get a straight line whose slope enables m to be calculated. If a close fit is obtained, it may be assumed that m is constant for the tube.

This method has been applied successfully to many viscosity-measurements, but apparently no attempt has been made in the case of a liquid metal, although in the latter case the effect of the correction is much more pronounced. The application of this procedure in the present work has been entirely successful.

The mean pressure head of the metal in the capillary. In calculating the pressure effective in producing flow through the capillary for the case in which the liquid is forced upwards through the capillary, the mean pressure head of the liquid metal must be subtracted from the applied manometric pressure. In general it is not sufficiently accurate to deduct from the applied pressure the arithmetic mean of the initial and final hydrostatic heads, especially when low velocities are used. In these

experiments the tube containing the volume V was of constant circular section, so that simple integration gives for the effective pressure

$$P = (h_2 - h_1) \rho g / \log_e \frac{H - h_1}{H - h_2} \quad \dots\dots(2),$$

h_1, h_2

where H is the applied pressure head and h_1 and h_2 are the initial and final hydrostatic heads of the metal in the capillary, all in centimetres of metal. This formula of course ignores the effect which the kinetic-energy correction has on the value of effective pressure.

The corresponding formula including this correction⁽⁷⁾ is

$$\frac{P}{\rho g} = H_1 + \frac{1}{4} K H_1^2 \quad \dots\dots(3),$$

H_1 where

$$H_1 = \frac{h_2 - h_1}{x_1 - x_2 + \log_e (x_1/x_2)},$$

$$x_1 = \sqrt{\{1 + K(H - h_1)\}} - 1,$$

$$x_2 = \sqrt{\{1 + K(H - h_2)\}} - 1,$$

K and

$$K = \frac{mg\rho^2 r^4}{16\eta^2 l^2}.$$

A comparison of the two formulae by a series of calculations shows that if K is sufficiently small the error introduced by the use of formula (2) can be ignored over a wide range of applied pressures. Taking h_1 and h_2 as approximately equal to 5.5 and 8.5 cm. respectively, the percentage difference between formulae (2) and (3) is negligibly small down to an applied pressure of about 9.0 cm., if K is less than 0.5. With the tubes employed in this work, for which K ranged from 0.18 to 0.33 for mercury, and from 0.02 to 0.04 for tin, the use of formula (2) gave sufficiently accurate values throughout.

The end correction. Allowance was made for the end effect by repeating the observations with the viscometer tube shortened by a known amount. The ratio of length to diameter was about 200, and the correction amounted to approximately 0.5 per cent.

§ 4. DESCRIPTION OF THE APPARATUS

Figure 1 shows the principal parts of the apparatus used.

Capillary apparatus. The capillary tube ab was 10 cm. long, with internal diameter about 0.05 cm. It opened into a wider cylindrical tube E , 10 cm. long with internal diameter 2.5 cm. The join between the capillary and its extension was such that the bore did not end abruptly, but was slightly funnel-shaped to facilitate linear flow.

Oxidation of the liquid metal was one of the most important difficulties to be met, since traces of surface impurity block the capillary and cause considerable variations in results. Oxidation was reduced by circulating hydrogen through the viscometer and by using a carbon vessel C as container for the tin. This container was supported on a spiral spring S to lessen the risk of breakage of the tube on expansion and contraction. The viscometers used were of Vitreosil transparent quartz.

The time of flow had to be recorded electrically and was determined by the use of platinum contacts Y_1 and Y_2 which defined the measured volume; the contacts and a wire dipping into the metal were connected to an electric timing circuit. The contacts were sealed into the ends of narrow conducting tubes.

The viscometer was fitted into the outer cylinder D , made of brass, by means of a heat-resisting ring, and the whole apparatus made gas-tight with a high-temperature cement.

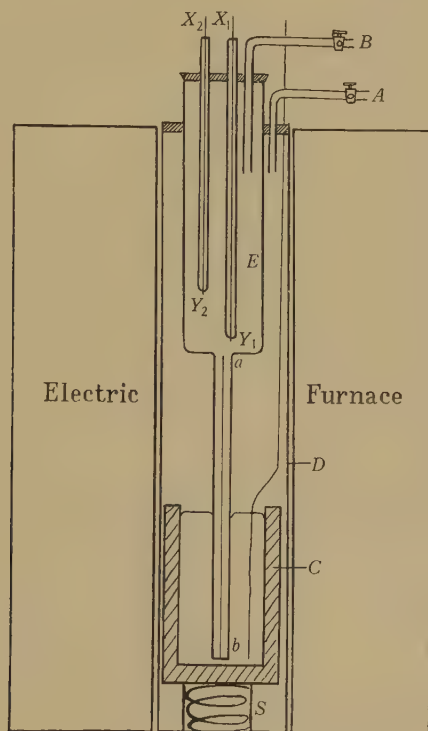


Figure 1. Capillary apparatus.

Pressure arrangement. On account of drainage and surface tension it was necessary to measure the time taken for the metal to fill the volume V rather than the time taken to empty it. The pressure-difference was usually obtained by sending hydrogen under pressure through tap A into the outer vessel. The hydrogen was subjected to this excess pressure by the use of a constant-pressure head device, which could itself be varied. In test experiments with mercury, however, where excess pressures up to 20 cm. of mercury were required, it was convenient to obtain part by reducing the pressure inside the capillary instead of applying the whole pressure to the outer vessel. For this purpose a water pump could be connected to the tap B through a 3-way tap. By using an additional 3-way tap it was possible to send hydrogen through the apparatus in both directions, and to apply excess or reduced pressure both inside and outside the capillary as required. By this means the possibility of the formation of surface oxide was considerably

reduced, and the movement of the liquid metal in the viscometer could be controlled more readily after each measurement. Two manometers were used differentially—a mercury manometer for pressures greater than 10 cm. of mercury, and a water manometer for smaller pressures.

Temperature-control and measurement. The apparatus was heated in an electric furnace 30 cm. long. Temperatures were measured by thermocouples of chromel-alumel, in conjunction with a precision potentiometer. One thermocouple was placed just above the surface of the metal in the container, and another as near as possible to the volume V between the contacts. Temperatures could be maintained constant to within $\frac{1}{2}^{\circ}\text{C.}$ for 2 or 3 hours, and to within $\frac{1}{10}^{\circ}\text{C.}$ for short periods.

§ 5. PROCEDURE

In all experiments hydrogen was circulated through the sealed apparatus during the whole process of heating and melting, and also between observations. The time of flow was recorded for a range of pressure-differences at each temperature, and each measurement was repeated three or four times. The hydrostatic heads h_1 and h_2 were determined at each temperature by noting the applied pressures necessary just to start the clock and just to stop the clock respectively. ht , where $h = P/\rho g$, was plotted against $1/t$ for each temperature.

§ 6. MEASUREMENTS ON MERCURY

The apparatus was tested with mercury in order to determine the accuracy for absolute measurements. Figure 2 shows the results for the two tubes used. It can

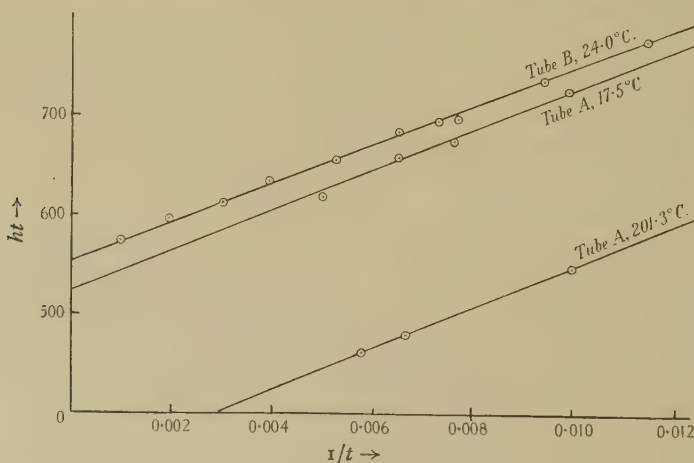


Figure 2. Results for mercury.

be seen that the points lie close to a straight line in each case, and consequently the magnitude of the kinetic-energy correction could be determined from the experiments.

The value of m obtained from figure 2 was 1.01 for tube A and 1.12 for tube B .

The values of the viscosity calculated from equation (1) for tube *A* are 0.0158₂ poise at 17.5° C. and 0.0099₄ poise at 200° C. Measurements with tube *B* were made at one temperature only and gave a mean value for η of 0.0153₈ poise at 24° C.; the results for this tube are shown in table 1.

Table 1. Results for mercury at 24° C. Tube *B*; radius 0.02549 cm.

Applied pressure (cm. of mercury)	Effective pressure (cm. of mercury)	Time (sec.)	Kinetic-energy correction	Viscosity (poises)
8.46	1.18	502.5	0.00103	0.01541
9.07	1.95	314.4	0.00164	0.01535
10.52	3.52	185.2	0.00279	0.01528
11.49	4.52	150.9	0.00342	0.01548
13.93	6.98	104.9	0.00492	0.01538
Mean				0.0153 ₈

The fact that the graphical method yielded a series of straight lines showed that, although the kinetic-energy correction was appreciable, the use of formula (2) with the effective pressures gave sufficiently accurate viscosity values.

MEASUREMENTS ON TIN; COMPARISON WITH OTHER AUTHORS

In view of the satisfactory results for mercury a comprehensive series of observations was made with tin over a range of temperature 235° C. to 330° C. The results are shown in figures 3 and 4. The points marked by crosses in figure 3 relate to measurements in which very inconsistent values of the time of flow were obtained. With tube *B*, individual time-measurements usually agreed to 1 part in 150 and showed that there was apparently little oxidation.

Table 2. Typical results for tin at 271° C. Tube *B*

Applied pressure (cm. of tin)	Effective pressure (cm. of tin)	Time (sec.)	Kinetic-energy correction	Viscosity (poises)
10.59	2.34	626.1	0.00047	0.01785
12.32	4.23	350.6	0.00085	0.01770
14.10	6.06	250.2	0.00118	0.01778
15.38	7.37	208.5	0.00142	0.01780
16.57	8.59	180.3	0.00164	0.01770
17.76	10.09	155.2	0.00191	0.01767
Mean				0.0177 ₅

Table 2 shows a typical set of results at a particular temperature; between 400 and 500 measurements were made in all. The effective pressures usually varied between about 2 cm. and 10 cm. of tin, and the time of flow ranged accordingly from 700 sec. to 120 sec. approximately. Plüss's smoothed values for the density of liquid tin were used; these are about 0.3 per cent higher than the figures used by

Sauerwald and Töpler. The accuracy obtained for the viscosity numbers is about 0.7 per cent.

Table 3 shows the variation of the viscosity of liquid tin with temperature; these mean values are taken from figure 5, which shows the comparison with the results obtained by Plüss, Sauerwald and Töpler, and Stott. The end correction is made only for the measurements with tube *B*, since tube *A* was broken early in the course of the work. The effects of expansion were negligibly small except for a small correction for the increase in length of the capillary tube.

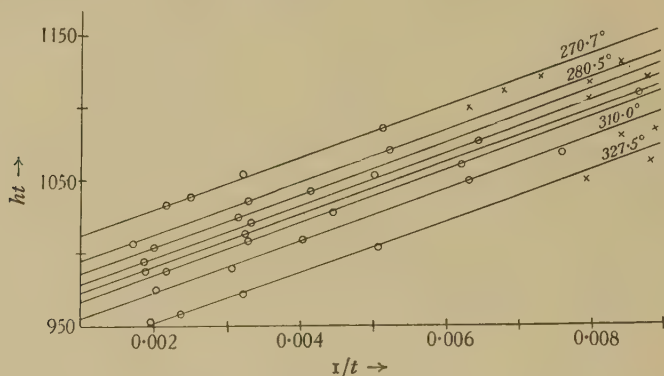


Figure 3. Results for tin, tube *A*.

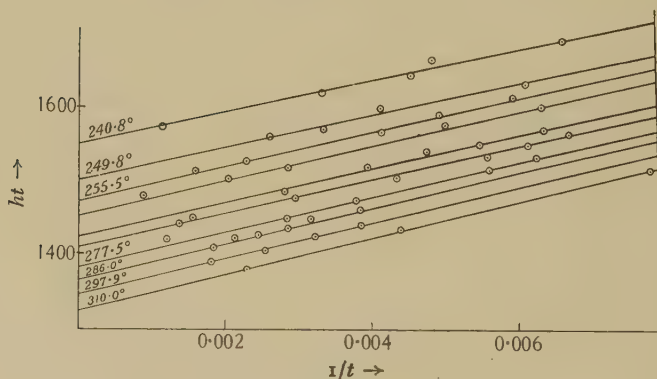


Figure 4. Results for tin, tube *B*.

Over the common range these results are from 3 to 7 per cent higher than those of Plüss. The curve cuts that of Sauerwald and Töpler a little above 300° C.; above this temperature, over the common range, the numbers are from 0 to 3 per cent higher, and below it they are from 0 to 1 per cent lower. The best agreement is with Stott's numbers, obtained with an oscillating disc; up to 300° C. the mean difference is less than 1 per cent. This agreement is all the more interesting in view of the fact that Stott's results are to a certain extent based on Sauerwald and Töpler's smoothed values. Undoubtedly the last-named authors' work was of great precision and it is difficult to find any source of systematic error in it. The

Table 3. Viscosity of liquid tin

Temperature (°C.)	Density (g./cm. ³)	Viscosity (poise)
235	6.967	0.0195
240	6.963	0.0192
250	6.958	0.0186
260	6.952	0.0181
270	6.946	0.0176
280	6.941	0.0173
290	6.934	0.0170
300	6.927	0.0167
310	6.920	0.0164
320	6.914	0.0162
330	6.909	0.0160

act shape of their curve, however, below 300° C. is difficult to ascertain, and it seems probable that the agreement of the present results with those of Stott is an indication of the general accuracy of Sauerwald and Töpler's measurements.

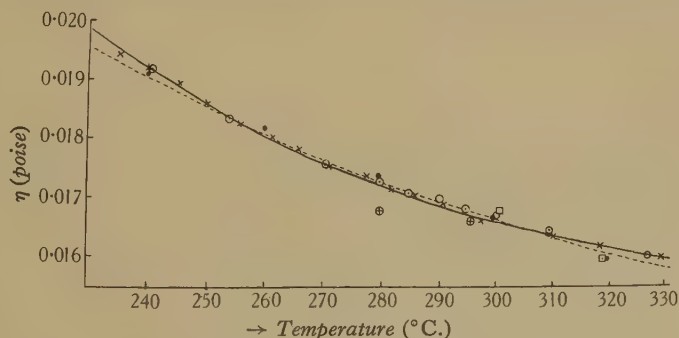


Figure 5. Stott: ●; broken curve. Sauerwald and Töpler: □. Plüss: ⊕.
Author: ⊙ tube A, × tube B, full curve.

§ 8. THE TEMPERATURE VARIATION OF VISCOSITY, AND THE VISCOSITY AT THE FREEZING-POINT

The temperature variation of the viscosity values shown in table 2 can be adequately expressed by the equation recently proposed by Andrade⁽⁸⁾:

$$\eta v^{\frac{1}{3}} = A e^{c/Tv},$$

where v is the specific volume, T is the absolute temperature, and A and c are arbitrary constants. This equation fits the experimental data very closely for a large number of organic liquids, and has been applied successfully in the case of

mercury. The greatest percentage difference between the experimental results for tin and the values calculated from the equation is -1.0 per cent, whilst the mean difference is 0.1 per cent. The agreement is very satisfactory since it is of the same order as the limit of experimental error.

The viscosity of liquid tin at the freezing-point, deduced from these experiments, is 0.0197 poise, as compared with Stott's value of 0.0195 poise, and Sauerwald and Töpler's extrapolated value of 0.020 poise. All these numbers are in good agreement with the value 0.019 poise calculated for tin according to Andrade's theory of the viscosity of liquids.

§ 9. CONCLUSION

The experiments show that the kinetic-energy correction can be determined experimentally, and consequently that absolute measurements of the viscosity can be made. The results indicate the general accuracy of the measurements made by Sauerwald and Töpler. Their data can therefore be used for calibration purposes in Stott's procedure for liquid metals, for which the flow method is not easily applicable.

§ 10. ACKNOWLEDGMENTS

The author is pleased to express his thanks to Prof. H. R. Robinson for his encouragement during the course of this work, undertaken in the physical laboratories of Queen Mary College; to Dr J. P. Andrews for his interest and suggestions throughout; and finally, to the Department of Scientific and Industrial Research and to Queen Mary College for grants in connexion with the work.

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DISCUSSION

Dr BRUCE CHALMERS. Comparatively small quantities of impurity are known to have a disproportionately large influence on some of the physical properties of metals. In particular, impurities that change the melting-point would be expected to affect the viscosity just above that point. It would increase the value of the paper if the author could give an analysis of the tin after use, that is, after it had taken up any free metal that may have been present in the carbon vessel.

AUTHOR'S reply. Various samples of tin were used in the measurements and in no case was the purity less than 99.5 per cent. Unfortunately no quantitative analysis of the impurities was made either before or after use.

621.396.674

ON THE CURRENT-DISTRIBUTION IN A LOOP AERIAL

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*Communicated by Prof. L. S. Palmer, July 9, 1935, and in revised form
August 16, 1935. Read in title November 15, 1935*

ABSTRACT. The work described in this communication is a continuation of a previous investigation on the current-distribution round a short-wave frame aerial. The present development deals with the determination of an expression for the amplitude of the current at any point in the aerial, and the resulting theoretical conclusions are tested by using a circular loop aerial of perimeter 11.3 m. The effect of damping is considered, and the probable value of the attenuation constant is calculated.

§ 1. INTRODUCTION

IN a recent investigation⁽¹⁾ into the properties of loop aerials when used with short waves, it was found desirable to have some information concerning the distribution of current. This is especially necessary when the ratio of the dimensions of the loop to the wave-length is of the order of unity because under these conditions the current varies greatly from point to point in the loop. Further, the non-uniformity of the current affects the radiation characteristics and hence, in order to obtain a proper understanding of the action of an aerial of this kind, it is desirable to know the exact current distribution and how this distribution is modified as the wave-length changes. It is for these reasons that the following work was undertaken.

§ 2. PREVIOUS WORK

A preliminary account of the work has already been given in a previous communication⁽²⁾. It was shown in that paper that when an incident wave or local oscillator actuates a loop aerial at a given point P , figure 1, the electric force causes a charge at P to oscillate to and fro at the frequency of the wave. The resulting disturbance travels round the loop with approximately the velocity of the wave in the surrounding medium and, by considering the disturbance propagated round and round the loop an infinite number of times in both directions, an expression was obtained giving the position and magnitude of the current antinodes.

It was deduced from the theory that (i) all the current antinodes are at a fixed distance from P , which is a fixed point determined by the position of the initial oscillation; (ii) the distribution of the nodes and antinodes round the loop is fixed in space, and in the case of a loop used as a receiver it is independent of the orientation

of the loop to the wave-front; (iii) the disposition of the current antinodes is symmetrical about the line PP' , figure 1; (iv) current antinodes always occur at P' irrespective of the wave-length; (v) successive current antinodes are $\frac{1}{2}n\lambda$, where n is an integer and λ is the wave-length, from P' measured in both directions round the loop.

In the previous paper a number of preliminary experiments which confirmed these results were described. It is the object of the present work to describe the

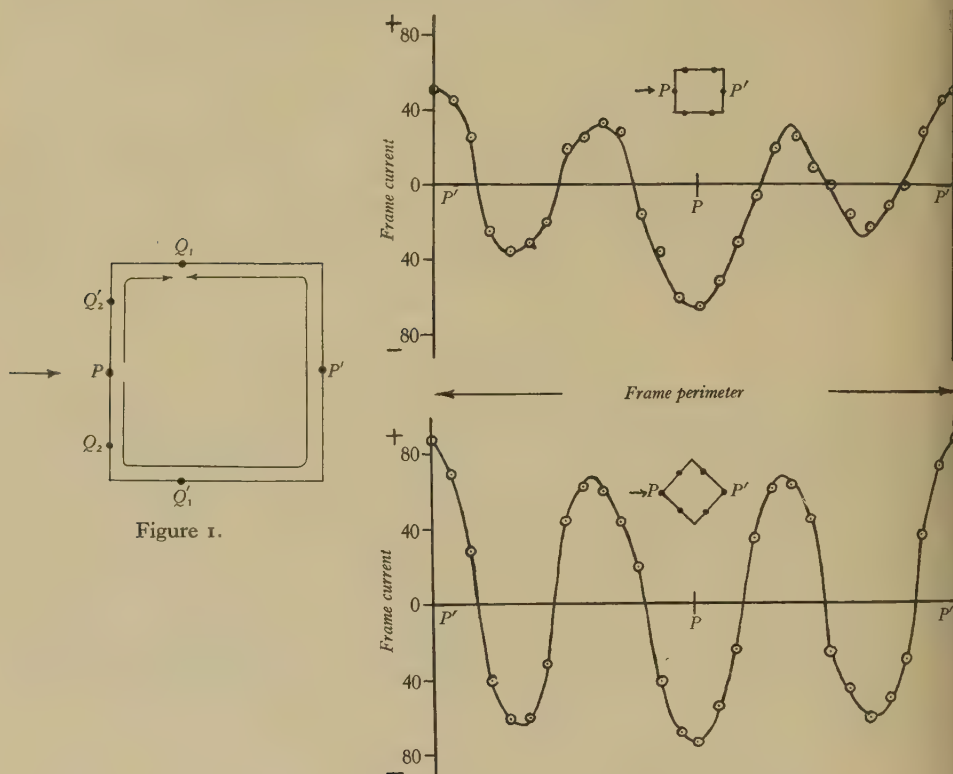


Figure 2. The current-distribution in the square and diamond positions. $\lambda = 3.74$ m., $l = 12.44$ m.

results of more detailed experiments, and to extend the theory so as to facilitate the experimental verification of certain deductions concerning the magnitude of the amplitude variations.

The preliminary experiments were carried out with a square frame and the current was measured with a thermojunction inserted in the frame wire. Figure 2 gives the results of some measurements made with a square frame of perimeter 12.44 m. on a wave-length of 3.74 m. The upper graph gives the current-distribution when the frame is oriented in the square position, i.e. with the wave-front parallel to one side of the frame, whilst the lower graph gives the current-distribution when the frame is oriented in the diamond position, i.e. with the

ave-front at 45° to the side of the frame. In each case the results are, within the limits of experimental error, in accordance with the deductions from the theory, but it is also apparent that although the waves remain fixed in space the current-distributions in the two cases are not exactly the same. This is because the actual current at any point of a rectangular frame depends not only on the initial effect arising from the circulation of electric waves round the frame-perimeter, but also on a supplementary effect due to reradiation between the parallel wires of the frame. In the case of a frame used for reception, this radiation effect is dependent on the orientation of the frame to the wave-front, and consequently the supplemental current due to this radiation may augment⁽³⁾ the initial current to different extents in the two cases, and so modify the current-distributions as shown in figure 2. To obviate this supplementary effect between the parallel limbs of a rectangular frame, it was decided that a circular loop aerial should be used in the present experiments, because with such a loop there are no parallel wires which can give rise to the disturbing radiation effects referred to above.

§ 3. THEORETICAL CONSIDERATIONS

In the theory given previously an expression giving the magnitude of the current at nodes was developed. The problem will now be considered from a different point of view and an expression will be calculated for the magnitude of the current at any point in the loop.

Consider a pair of transmission lines of length $\frac{1}{2}l$ connected to a generator at one end and short-circuited at the other. If the primary constants of the line are R , L , C and G per unit length, then it can be shown⁽⁴⁾ that

$$I_g = \frac{V_g}{Z_0} \coth \frac{1}{2} Pl \quad \dots\dots(1),$$

where I_g and V_g represent the current and voltage in the line as measured at the generator, Z_0 is the (complex) characteristic impedance, and $P = \alpha + j\beta$, where α is the attenuation constant, β is the wave-length constant and j is $\sqrt{-1}$.

It follows from equation (1) that the current at a point in the line at a distance x from the generator is given by

$$I_x = \frac{V_g}{Z_0} \operatorname{cosech} \frac{1}{2} Pl \cosh P \left(\frac{1}{2} l - x \right) \quad \dots\dots(2).$$

This equation can be used for calculating the amplitude of the current at any point in the loop.

In the analysis given above the e.m.f. induced at the point P has alone been considered, whilst in actual fact a second e.m.f. induced at the point P' might have been expected. However, the experimental results of the previous papers show that this second e.m.f. is of negligible importance in determining the current-distribution. This may be seen by referring to figure 6 of the paper by Palmer, Taylor and Witty⁽²⁾ and figure 3 of the paper by Palmer and Witty⁽³⁾. In both these cases if the effect of the e.m.f. induced at P' had been appreciable, then additional current

l

R, L, C, G

I_g, V_g
 Z_0, P, α
 β, j
 x

antinodes, symmetrically placed with respect to those actually observed, would have been present.

Equation (2) will now be used to determine the variation of the current at a number of selected points in the loop.

At the point P , see figure 1, $x=0$,

$$I_P \quad \therefore I_P = I_0 \operatorname{cosech} \frac{1}{2}Pl \cosh \frac{1}{2}Pl = I_0 \coth \frac{1}{2}Pl \quad \dots\dots(3).$$

At the point P' , $x=\frac{1}{2}l$,

$$I_{P'} \quad \therefore I_{P'} = I_0 \operatorname{cosech} \frac{1}{2}Pl \quad \dots\dots(4).$$

Equations* (3) and (4) give respectively the variation in the amplitude of the current at the points P and P' as the wave-length is changed. The experimental verification of these expressions is difficult because if the loop be used as a receiver the radiation field must be kept constant as the wave-length changes, and this is sometimes impossible except over a very limited range of wave-lengths. For this reason it is desirable to calculate a theoretical expression for the current ratio $I_P/I_{P'}$, and then the experimental value of this ratio will be independent of the absolute values of the currents, and therefore of the field which produces them. Consequently the experimental value of this ratio may be compared with the theoretical value even though the field-strength varies slightly with change of wave-length.

From equations (3) and (4)

$$\begin{aligned} I_P/I_{P'} &= \cosh \frac{1}{2}Pl \\ &= \cosh \frac{1}{2}(\alpha + j\beta)l \\ &= \cosh \frac{1}{2}\alpha l \cos \frac{1}{2}\beta l + j \sinh \frac{1}{2}\alpha l \sin \frac{1}{2}\beta l \quad \dots\dots(5). \end{aligned}$$

The graph of this equation can be plotted by considering each expression separately, and then adding the two expressions together vectorially. This has been done and is shown by the full-line graph in figure 3. If damping be neglected, i.e. if $\alpha=0$, the equation becomes

$$I_P/I_{P'} = \cosh \frac{1}{2}j\beta l = \cos \frac{1}{2}\beta l \quad \dots\dots(6)*.$$

The graph of equation (6) is given in figure 3 by the dotted curve, and it is apparent that the effect of damping is to raise the value of the current ratio $I_P/I_{P'}$ by $\cosh \frac{1}{2}\alpha l$

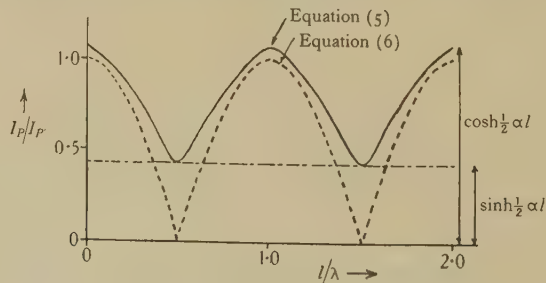


Figure 3. The variation of $I_P/I_{P'}$ with wave-length.

when $l/\lambda=0, 1.0, 2.0$, etc., and by $\sinh \frac{1}{2}\alpha l$ when $l/\lambda=0.5, 1.5, 2.5$, etc., although the general shape of the graph is similar to that obtained if damping is neglected.

* If damping be neglected these expressions become $I_P = I_0 \cot \frac{1}{2}Pl$ and $I_{P'} = I_0 \operatorname{cosec} \frac{1}{2}Pl$, which follow directly from equation (5) of the previous paper⁽²⁾.

The experiments which were carried out to test the above theory will now be considered.

§ 4. EXPERIMENTAL WORK

Experiments were carried out with a circular loop aerial of perimeter 11.3 m. The aerial wire was carried on suitable insulators attached to the supporting framework, and the framework itself was fixed on rollers so arranged that the aerial could be rotated about a fixed central axis. The current was measured by means of a

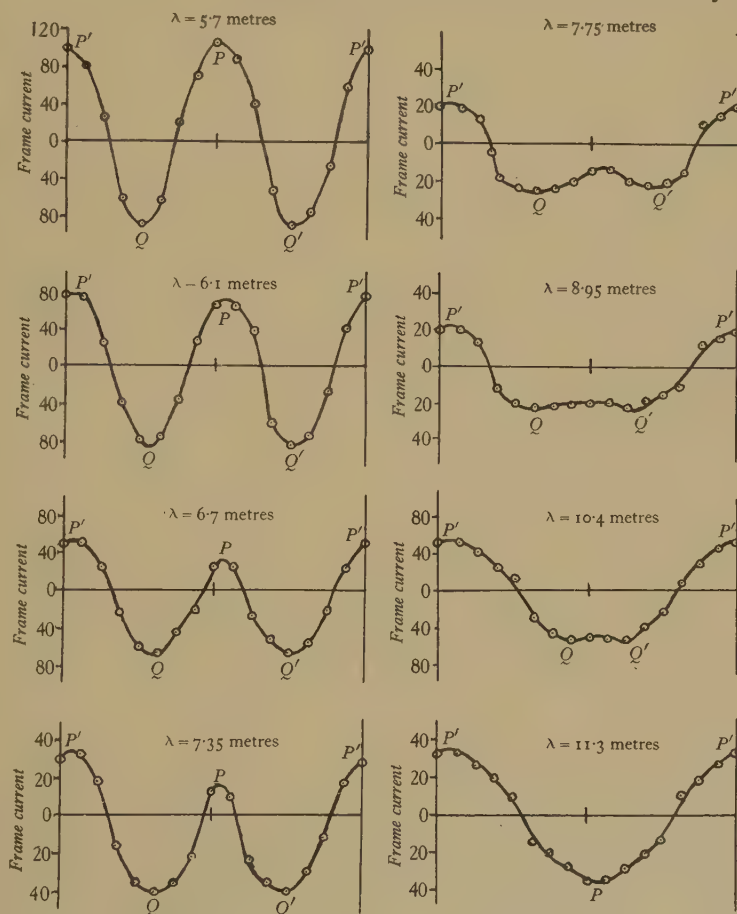


Figure 4. The current-distribution in a circular loop aerial of perimeter 11.3 m., with various wave-lengths.

vacuum thermojunction and a microammeter. Where the thermojunction was inserted in the loop, the aerial wire was shunted by a condenser of capacity $0.0005 \mu\text{F}$. which tuned that portion of the loop to the wave-length in use. The current in the shunted portion of the aerial wire varied in the same way as that in adjacent parts of the loop but was of greater magnitude, and was consequently easier to measure. The thermojunction was connected by a short length of flex to a microammeter which rested on a small platform attached to the frame.

The transmitter consisted of an ordinary series-fed Hartley circuit. To this was coupled a Hertzian dipole aerial of adjustable length. In the actual experiments the transmitter was arranged several wave-lengths away from the receiving loop, the current in which was measured at various points along the perimeter. Figure 4 shows a series of results obtained in this way, with wave-lengths varying from 5.7 to 11.3 m.

§ 5. DISCUSSION OF RESULTS

Examination of these curves shows that the current-distribution is in accordance with the theoretical predictions given in § 2. With a wave-length of 5.7 m., four peaks occur. This is to be anticipated from the theory, because under these conditions l/λ is approximately equal to 2. As the wave-length increases the magnitude of the current at the point P gradually decreases until, with a wave-length of 7.35 m., the peak at this point almost disappears. Further increase of the wave-length causes the peak to disappear completely, and the two neighbouring peaks Q and Q' move closer and closer together until, with a wave-length of 11.3 m., the two peaks merge into one, and only two current antinodes are obtained round the perimeter, one at the point P and one at the point P' . This transition with increase of wave-length is in accordance with the theory. The current antinodes at Q and Q' are always $\frac{1}{2}\lambda$ from P' measured round the perimeter of the loop, and hence the antinodes at Q and Q' will gradually move further from P' until, when $l/\lambda = 1$, only the antinodes at P and P' are obtained. Still further increase of wave-length causes the current antinode at P to disappear again, and eventually the current becomes approximately uniform throughout the entire loop.

These current-variations will now be compared with those predicted by the theory developed in § 3. This may be done by calculating the current ratio $I_P/I_{P'}$ for each of the curves given in figure 4. The requisite data are given in the table below.

Wave-length λ (metres)	I_P	$I_{P'}$	Ratio $I_P/I_{P'}$	l/λ
5.7	106	100	1.06	1.98
6.1	72	76	0.95	1.91
6.7	56	32	0.57	1.68
7.35	34	16	0.47	1.54
7.75	23	12	0.52	1.46
8.95	23	19	0.82	1.26
10.4	52	48	0.92	1.09
11.3	37	36	1.03	1.00

In figure 5 the experimental values of $I_P/I_{P'}$ are plotted against l/λ , and on the same graph the theoretical curve given by equation (5) has been plotted with an attenuation constant equal to 0.073 per metre.

§ 6. CONCLUSIONS

The results of the above experiments seem to constitute further evidence in support of the theory outlined in this paper and in the previous communication,

both with regard to the positions round a loop aerial at which current antinodes occur, and also with regard to the magnitude of the amplitude-variations which occur with changes of wave-length. Furthermore it has been shown that with these

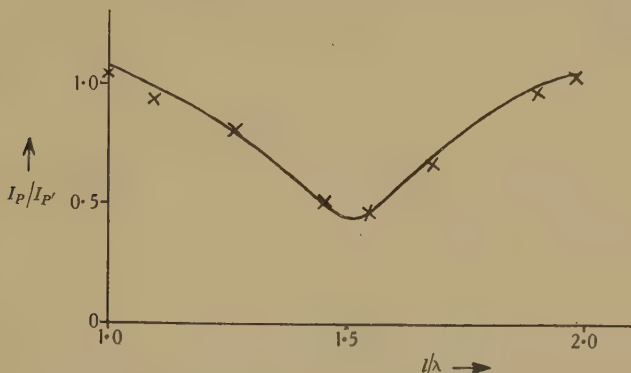


Figure 5. Experimental values (crosses) of the ratio $I_P/I_{P'}$ compared with the theoretical values from equation (5) (smooth curve).

short waves it is necessary to take damping into consideration if the theoretical calculations are to be comparable with the experimental measurements.

Hence it is concluded that equation (2) gives the positions as well as the magnitudes of the current antinodes round a short-wave loop aerial actuated by an e.m.f. located at one point, and this equation may be used for calculating the current-distribution in a loop aerial when the wave-length and position of the applied e.m.f. are known.

§ 7. ACKNOWLEDGMENT

Finally my most sincere thanks are due to Prof. L. S. Palmer for continual interest and invaluable suggestions during the course of the work.

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TEMPERATURE-RISE IN A MATERIAL OF WHICH THE THERMAL PROPERTIES VARY WITH TEMPERATURE

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ABSTRACT. The partial differential equations governing the flow of heat in a medium for which the thermal conductivity and volumetric specific heat vary parabolically with temperature is reduced to an ordinary differential equation for the case when the medium is semi-infinite in extent. The equation is solved exactly for the case where the two properties vary proportionally to each other, and approximately, in powers of $x/\sqrt{(2t)}$, where x is the distance from the hot face and t the time, for the general case.

§ 1. INTRODUCTORY

THE fundamental equation for the temperature-distribution in a material of which the thermal conductivity and specific heat vary with temperature is found, by the usual process of equating the net heat-inflow over the boundaries of an element of volume to the product of the temperature-rise and heat-capacity, to be

$$c \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left(K \frac{\partial \theta}{\partial x} \right) + \frac{\partial}{\partial y} \left(K \frac{\partial \theta}{\partial y} \right) + \frac{\partial}{\partial z} \left(K \frac{\partial \theta}{\partial z} \right) \dots\dots(1),$$

where θ is the temperature at time t and at the point (x, y, z) , K is the thermal conductivity and c the specific heat per unit volume.

This equation is non-linear, and hence it is impossible to obtain a general solution by the addition of particular solutions. Thus the solution adapted to any but the very simplest boundary conditions would be overwhelmingly difficult to obtain. Nevertheless, it appears of interest to consider in detail some specific case in order to ascertain the relative importance of the various factors involved. From such an analysis, it should be possible to assess, in other more complicated cases, what deviation from the simple solution pertaining to unvarying properties is to be expected.

§ 2. REDUCTION TO AN ORDINARY DIFFERENTIAL EQUATION

The simplest case which suggests itself is that of the one-dimensional flow of heat in a large mass of material initially at the uniform temperature θ_0 , the plane face of which is raised when the time $t=0$ to a temperature θ_1 and maintained at

is temperature thereafter. We take this plane to be the plane $x=0$, and the equation reduces to

$$c \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left(K \frac{\partial \theta}{\partial x} \right) \quad \dots\dots(2).$$

It is known that, if K and c are independent of θ , the solution of this equation under the conditions stated is

$$\theta = \theta_1 + \frac{2(\theta_0 - \theta_1)}{\sqrt{\pi}} \int_0^{x/2h\sqrt{t}} e^{-\beta^2} d\beta, \text{ where } h^2 \text{ is the thermal diffusivity } K/c. \quad h$$

Adopting the suggestion contained in this solution, we take a new variable y equal to $x/(2t)^{\frac{1}{2}}$ and transform equation (2) by its aid into an ordinary, instead of a partial, differential equation, θ becoming a function of y only. We have

$$\frac{\partial \theta}{\partial t} = -\frac{x}{(2t)^{\frac{3}{2}}} \frac{\partial \theta}{\partial y} \quad \text{and} \quad \frac{\partial \theta}{\partial x} = \frac{1}{(2t)^{\frac{1}{2}}} \frac{\partial \theta}{\partial y},$$

so that equation (2) becomes

$$-\frac{xc(\theta)}{(2t)^{\frac{3}{2}}} \frac{d\theta}{dy} = \frac{1}{(2t)^{\frac{1}{2}}} \frac{d}{dy} \left[K(\theta)(2t)^{-\frac{1}{2}} \frac{d\theta}{dy} \right],$$

$$-\frac{xc(\theta)}{(2t)^{\frac{3}{2}}} \frac{d\theta}{dy} = K(\theta) \frac{d^2\theta}{dy^2} + \frac{dK}{d\theta} \left(\frac{d\theta}{dy} \right)^2 \quad \text{since} \quad \frac{dK(\theta)}{dy} = \frac{dK(\theta)}{d\theta} \frac{d\theta}{dy}.$$

The equation for θ as a function of y is thus

$$yc d\theta/dy + K d^2\theta/dy^2 + (dK/d\theta) (d\theta/dy)^2 = 0 \quad \dots\dots(3),$$

where c , K and $dK/d\theta$ are functions of θ .

§ 3. FURTHER REDUCTION TO A PARTICULAR CASE

It does not seem possible to solve this equation in general, and empirical expressions for K and c as functions of θ must therefore be introduced. It is probably sufficiently general if we write

$$c = c_0(1 + \alpha\theta + \beta\theta^2) \quad \text{and} \quad K = K_0(1 + \gamma\theta + \delta\theta^2). \quad c_0, K_0, \alpha, \beta, \gamma, \delta$$

Equation (3) then takes the form

$$yc_0(1 + \alpha\theta + \beta\theta^2) d\theta/dy + K_0(1 + \gamma\theta + \delta\theta^2) d^2\theta/dy^2 + K_0(\gamma + 2\delta\theta) (d\theta/dy)^2 = 0.$$

From the point of view of dimensional homogeneity it is preferable to make a further substitution and put y equal to $h_0 z$, where $h_0^2 = K_0/c_0$, since the new variable z is dimensionless. The equation then becomes

$$z(1 + \alpha\theta + \beta\theta^2) \theta' + (1 + \gamma\theta + \delta\theta^2) \theta'' + (\gamma + 2\delta\theta) \theta'^2 = 0 \quad \dots\dots(4), \quad \theta'$$

where primes denote differentiations with respect to z .

§ 4. EXACT SOLUTION IN A PARTICULAR CASE

This equation is still intractable, and apparently can only be solved by approximate methods. Before carrying out this process, however, it is interesting to notice that it can be solved exactly in one case, namely if the conductivity and specific

heat both vary linearly at the same rate, so that the diffusivity remains constant. In these circumstances $\beta = \delta = 0$, whilst $\alpha = \gamma$. Thus equation (4) reduces to

$$(z\theta' + \theta'')(1 + \alpha\theta) + \alpha\theta'^2 = 0.$$

The quantity $e^{z^2/2}$ is an integrating factor for this equation. On multiplying the latter by its integrating factor, we can write it

$$\frac{d}{dz} [e^{z^2/2} (1 + \alpha\theta) \theta'] = 0,$$

i.e.

$$(1 + \alpha\theta) d\theta = A e^{-z^2/2} dz,$$

A, B

whence

$$(1 + \alpha\theta)^2 / 2\alpha = B + A \int_0^z e^{-z^2/2} dz \quad \dots\dots(5),$$

which gives an explicit expression for θ as a function of z , where $z = x/h_0 (2t)^{1/2}$.

It is of distinct interest to notice that although the diffusivity is constant, the temperature-distribution differs from that which is obtained when the conductivity and specific heat separately are constants.

§ 5. SOLUTION IN THE GENERAL CASE

In the general case, equation (4) must be solved by approximate methods. Since it is of the second order there are two arbitrary constants in the solution. These we fix by writing $\theta = 0$ when $z = 0$ and $d\theta/dz = \lambda$ when $z = 0$.

Successive differentiations of equation (4) with respect to z give a series of equations of which the fourth is

$$\begin{aligned} 16(\alpha + 2\beta\theta) \theta' \theta''' + 4(1 + \alpha\theta + \beta\theta^2) \theta^{1v} + 48\beta\theta'^2 \theta'' + 30\beta z \theta' \theta''^2 \\ + 20\beta z \theta'^2 \theta''' + 12(\alpha + 2\beta\theta) \theta''^2 + 10z(\alpha + 2\beta\theta) \theta'' \theta''' + 5z(\alpha + 2\beta\theta) \theta' \theta^{1v} \\ + z(1 + \alpha\theta + \beta\theta^2) \theta^v + 30\delta \theta'^3 + 120\delta \theta' \theta'' \theta''' + 30\delta \theta'^2 \theta^{1v} + 10(\gamma + 2\delta\theta) \theta'''^2 \\ + 15(\gamma + 2\delta\theta) \theta'' \theta^{1v} + 6(\gamma + 2\delta\theta) \theta' \theta^v + (1 + \gamma\theta + \delta\theta^2) \theta^{v1} = 0. \end{aligned}$$

Inserting the boundary conditions into these equations in turn, and using the subscript zero for values at $z = 0$, we find that

$$\theta_0 = 0, \quad \theta_0' = \lambda, \quad \theta_0'' + \gamma\lambda^2 = 0,$$

$$\lambda + 3\gamma\lambda\theta_0'' + \theta_0''' + 2\delta\lambda^3 = 0,$$

$$2\alpha^2 + 2\theta_0'' + 12\delta\lambda^2\theta_0'' + 3\gamma\theta_0''^2 + 4\gamma\lambda\theta_0''' + \theta_0^{1v} = 0,$$

$$3\theta_0''' + 6\beta\lambda^3 + 9\alpha\lambda\theta_0'' + 30\delta\lambda\theta_0''^2 + 20\delta\lambda^2\theta_0''' + 10\gamma\theta_0''\theta_0''' + 5\gamma\lambda\theta_0^{1v} + \theta_0^v = 0,$$

$$16\alpha\lambda\theta_0''' + 4\theta_0^{1v} + 48\beta\lambda^2\theta_0'' + 12\alpha\theta_0''^2 + 30\delta\theta_0''^3 + 120\delta\lambda\theta_0''\theta_0'''$$

$$+ 30\delta\lambda^2\theta_0^{1v} + 10\gamma\theta_0'''^2 + 15\gamma\theta_0''\theta_0^{1v} + 6\gamma\lambda\theta_0^v + \theta_0^{v1} = 0.$$

These equations can now be solved for the successive derivatives of θ , giving

$$\theta_0 = 0, \quad \theta_0' = \lambda, \quad \theta_0'' = -\gamma\lambda^2, \quad \theta_0''' = -\lambda + (3\gamma^2 - 2\delta)\lambda^3,$$

$$\theta_0^{1v} = (6\gamma - 2\alpha)\lambda^2 + (20\gamma\delta - 15\gamma^3)\lambda^4,$$

$$\theta_0^v = 3\lambda + (26\delta - 49\gamma^2 - 6\beta + 19\alpha\gamma)\lambda^3 + (40\delta^2 - 210\gamma^2\delta + 105\gamma^4)\lambda^5,$$

$$\theta_0^{v1} = (24\alpha - 52\gamma)\lambda^2 + (92\alpha\delta + 84\beta\gamma - 576\gamma\delta + 504\gamma^3 - 204\alpha\gamma^2)\lambda^4$$

$$+ (2520\gamma^3\delta - 945\gamma^5 - 1120\gamma\delta^2)\lambda^6.$$

The final solution valid for sufficiently small values of z is then obtained from Laplace's theorem by substituting the above values of $\theta_0^{(v)}$ in the expression

$$\theta = \theta_0 + z\theta_0' + \frac{z^2}{2!}\theta_0'' + \frac{z^3}{3!}\theta_0''' + \frac{z^4}{4!}\theta_0^{IV} + \frac{z^5}{5!}\theta_0^V + \frac{z^6}{6!}\theta_0^{VI} + \dots$$

The terms are rearranged in powers of λ , this expression becomes

$$\theta = \lambda \left[z - \frac{z^3}{6} + \frac{z^5}{40} + \dots \right] + \text{terms in } \lambda^2, \lambda^3, \dots$$

The expression in the bracket represents the expansion of $\lambda \int_0^z e^{-z^2/2} dz$, i.e. the temperature which would be reached in the case where the thermal constants are independent of temperature.

Thus the result reached might be written in the form

$$\theta = \lambda \int_0^z e^{-z^2/2} dz + \text{terms in } \lambda^2, \lambda^3, \dots,$$

the terms after the first representing the disturbance in θ due to the variation of thermal conductivity and specific heat with temperature. It is worthy of note that the variation of the conductivity has a much greater effect than that of the specific heat; this is evidenced by the fact that α and β are absent from the terms in $\lambda^2 z^2$ and in $\lambda^3 z^3$, the former first making its appearance in the term in $\lambda^2 z^4$ and the latter in $\lambda^3 z^5$.

§ 6. NUMERICAL ILLUSTRATION

As an illustration we take the case of a brick for which $h_0^2 = 0.0020$ and both specific heat and thermal conductivity increase by 1 per cent per 1°C . The final temperature, reached when $z = 0$, is taken as the zero of temperature, and the rise of the hot face is determined by $\lambda = 200/\sqrt{(2\pi)}$, which makes the dominating term due to the value 100 when $z = \infty$. Thus the initial temperature would be 100°C . If there were no variation of the thermal constants with temperature. The whole expression in this case reduces to

$$\begin{aligned} \theta &= \frac{200}{\sqrt{(2\pi)}} \int_0^z e^{-z^2/2} dz - \frac{100}{\pi} z^2 + \frac{79.95 z^3}{\pi} + \frac{33.33 z^4}{\pi} - \frac{25.0 z^4}{\pi^2} - \frac{39.9 z^5}{\pi} \\ &\quad + \frac{279.4 z^5}{\pi^2} - \frac{7.778 z^6}{\pi} + \frac{166.67 z^6}{\pi^2} - \frac{105.0 z^6}{\pi^3} + \dots \\ &= \frac{200}{\sqrt{\pi}} \int_0^{z/\sqrt{2}} e^{-x^2} dx - 31.831 z^2 + 25.43 z^3 - 14.74 z^4 + 15.63 z^5 - 19.45 z^6 + \dots \end{aligned}$$

The numerical values calculated from this formula are given in table 1 for a selection of values of z . The expansion is only convergent for $z < 1$ and appears to be of adequate accuracy up to about $z = 0.6$; beyond this point it would be necessary to carry it to higher powers of z .

Table 1

z	$\frac{200}{\sqrt{\pi}} \int_0^{z/\sqrt{2}} e^{-x^2} dx$	Sum of remaining terms
0.005	0.40	-0.00079
0.01	0.80	-0.00316
0.02	1.60	-0.0125
0.05	3.99	-0.0765
0.10	7.97	-0.2943
0.20	15.85	-1.090
0.40	31.08	-3.76
0.60	45.14	-7.58

It will be seen that the deviation in the temperature-distribution does not become 1 per cent of the whole temperature-rise until $z=0.02$.

With a value 0.0020 of h_0^2 , a typical value for a refractory material, this occurs when $x/\sqrt{t}=0.06$. Thus at a depth of 5 cm. no deviation will exist after about $1\frac{1}{2}$ hours, whilst conversely, after say 4 hours, the deviation is only to be found at distances from the hot face greater than 7 cm.

It is also worthy of remark that the values of the temperature calculated by means of the series expansion are hard to compare directly with those obtained from the exact formula (5) which applies to this case.* This arises from the fact that the series expansion is divergent beyond $z=1$, and consequently the constant λ cannot be adjusted to give a specified range of temperature; only the dominant term can be caused to vary over a selected range, and thus the solution represented by the series in fact covers some slightly different range. In the case of the exact solution the adjustment of the constants A and B causes the actual temperature to vary over the range desired.

Nevertheless it is of interest to compare the exact solution with that tabulated above. In table 2, the constant B of equation (5) has been taken as 50, and three values—100, 106.2 and 114.5—have been assigned to $A\sqrt{(\pi/2)}$.

Table 2. Temperature as function of z , where $z=x/h_0\sqrt{(2t)}$

z	Temperature			
	By series expansion	By formula (2), $A\sqrt{(\pi/2)}$ being taken as		
		106.2	114.5	100
0.005	0.40	0.4	0.4	0.40
0.01	0.80	0.8	0.9	0.80
0.02	1.59	1.7	1.8	1.60
0.05	3.92	4.1	4.5	3.99
0.10	7.70	8.1	8.7	7.67
0.20	14.76	15.6	16.8	14.76
0.40	27.32	28.8	30.8	27.43
0.60	37.58	40.0	42.6	37.92

* See, however, the author's reply to the discussion, page 124.

§ 7. CONCLUSIONS

Although the illustrative example just given is one in which the variation of both properties is relatively rapid, yet the deviations from the case of constant diffusivity are fairly small. This may in part be due to the fact that the specific heat and thermal conductivity in this example are proportional to each other, so that their ratio remains constant.

We therefore take another example less likely to be encountered in practice, in which the specific heat increases by 1 per cent per 1° C., but the conductivity decreases by 1 per cent per 1° C.

In this case, the series formula becomes

$$\theta = \frac{200}{\sqrt{\pi}} \int_0^{z/\sqrt{2}} e^{-x^2} dx - 31.831z^2 + 25.43z^3 + 4.11z^4 - 0.47z^5 + 0.75z^6 \dots,$$

and the sum of the last five terms varies with z in the way shown in table 3.

Table 3

z	Sum of terms other than dominating term
0.005	-0.00079
0.01	-0.0032
0.02	-0.0125
0.05	-0.0764
0.10	-0.292
0.20	-1.064
0.40	-3.36
0.60	-5.43

Here also, the deviations from the case of constant diffusivity are fairly small, and it seems therefore reasonable to assume that a similar result would hold in the cases likely to be encountered in practice.

DISCUSSION

Mr C. R. DARLING said that the paper had a bearing on the problem of the time taken by the centre of a block of metal in a furnace to attain a steady temperature. Experimenting with thermocouples on cylindrical blocks of steel he had found that the time varied as the square of the diameter; this appeared to agree with Mr Awbery's conclusions.

Mr E. D. VAN REST. I am sometimes asked to make calculations of the rise of temperature inside a piece of wood when it is subject to given external conditions, for instance in a drying chamber. My early measurements of thermal diffusivity were not entirely in agreement with theory and at one time I thought that the discrepancies might be due to a temperature variation of the diffusivity. This proved not to be the case, for fair agreement with theory was later obtained. This

is in accord with the author's findings that the temperature variation does not cause large differences. I am interested, too, in the conclusion arrived at in § 2 where the author shows that the same proportionate variation in conductivity and specific heat, while not affecting their ratio, the diffusivity, does affect the temperature-distribution. The conclusion is, I suppose, that measurements of the temperature variation of diffusivity cannot be used to calculate how the temperature-distribution differs from that predicted from simple theory, but must give place to separate measurements of conductivity and specific heat. With wood, one of the difficulties in applying theory to practice is the probably large variation of diffusivity with moisture-content combined with the uneven distribution of moisture during drying.

AUTHOR'S reply. In reply to Mr Darling and Mr van Rest, I am interested to learn that their experiments are not in contradiction to the theory. Fortunately, the practical importance of the point raised in § 2 is small, since the numerical calculations show that the deviation of the temperature-distribution from that given by simple theory is never likely to become serious.

I am indebted to Prof. Davidson for pointing out an algebraical error which affects the numerical values in tables 1, 2 and 3 as printed in the advance proofs. The necessary corrections have now been made.

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A NEGATIVE-RESISTANCE OSCILLATOR

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TRACT. It is shown that an amplifier with its input and output terminals connected either can behave as a negative resistance. This principle leads to the design of an oscillator employing two triodes, and having certain advantages over both the ordinary reaction circuit and the screen-grid dynatron. Some special wave-forms which were observed are illustrated. A method of using the instrument to measure the dynamic resistance of an oscillatory circuit is suggested.

§ 1. INTRODUCTION

METHODS of generating electrical oscillations by means of thermionic valves may be divided broadly into two classes. In the first class are the reaction methods in which some coupling is provided between the grid and anode circuits. This is often a mutual-inductance coupling or reaction coil, but we may also include in the same class methods in which the coupling is effected by using a tap on the tuning inductance, or by splitting the tuning condenser into two condensers in series. The second class consists of the negative-resistance methods, in which use is made of the fact that under certain conditions a pair of electrodes can be found for which the curve of current against voltage has a negative slope over part of its range, so that the system is capable of delivering power to an external circuit. The phenomenon of secondary emission causes the plate current of a triode to follow a curve of this sort when the grid is maintained at a large positive potential with respect to the filament. A valve used in this way is usually known as a *dynatron*. In the case of a reaction circuit the operation of the valve in conjunction with a given coupling can be represented by means of an oscillation characteristic showing a negative slope⁽¹⁾. Analytically therefore the two classes are similar, and there is no fundamental distinction between them. There is however an important difference in practice. In the second class of circuit the valve and its associated apparatus, such as batteries, can be connected to the oscillatory circuit proper by two wires only, without the complications of reaction coils, tapped inductances or split condensers. This is particularly convenient when operation is required over a wide range of frequencies, since the number of connexions to be changed and adjustments to be made is reduced to a minimum.

When a triode is used as a dynatron the large potential which must be applied to the grid produces a very large emission current. This results in a heavy consumption of power, overheating of the grid, and deterioration of the emitting surface; the last effect is particularly serious in the case of the oxide-coated cathodes used in

modern valves. It is therefore usual to employ a screen-grid valve with the outer or screening grid maintained at a high positive potential and the inner or control grid connected to the filament or cathode. This arrangement is deservedly popular, but suffers nevertheless from several disadvantages. Thus (i) the valve usually has to be specially selected; (ii) the working conditions are fairly critical and apt to vary with time; (iii) it is not possible to obtain low values of negative resistance, so that the oscillatory circuits must be of low damping; (iv) two separate high-tension voltages are required; (v) the oscillatory circuit is at a high d.-c. potential with respect to the filament; and (vi) the d.-c. component of the anode current passes through the inductance of the oscillatory circuit, which is objectionable if iron-cored inductances are to be used.

The circuit to be described makes use of two valves, which can be triodes, operating under normal amplifying conditions. It has the advantages of the negative-resistance type of oscillator without the above-mentioned disadvantages of the screen-grid dynatron.

A circuit using two triodes to give a negative resistance effect has been described under the name of *kallirotron* by L. B. Turner⁽²⁾. It is unsuitable for general use as an oscillation-generator, since it makes use of five batteries at different oscillatory potentials. Again, a circuit apparently very similar to that described below has been used by C. S. Franklin as the master-oscillator of short-wave transmitters⁽³⁾. The present paper shows how the fundamental principle made use of by Turner and by Franklin can be applied to the design of a universal oscillator which can operate at any desired frequency, and in which the magnitude of the negative-resistance effect is completely under control.*

§ 2. THE AMPLIFIER AS A NEGATIVE RESISTANCE

Figure 1 represents an amplifier with input terminals a, b and output terminals c, d . It is assumed that the internal connexions are such that one of the input and

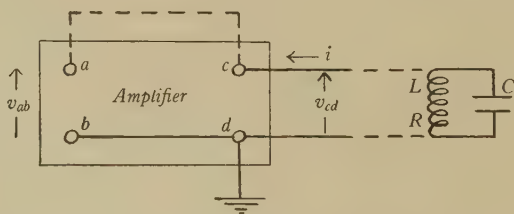


Figure 1. An amplifier used as a negative resistance.

one of the output terminals are held at the same potential, and the points b, d are accordingly shown connected together and to earth. The dotted lines should be ignored for the moment.

* During the preparation of this paper, a paper on "A negative-resistance device and its application to harmonic analysis" was read by Mr C. W. Oatley before the Physical Society, *Proc. phys. Soc.* 47, 471 (1935). The present author's arrangement can of course be used for the same purpose as Mr Oatley's, and it appears to have some practical advantages over his circuit.

If v_{ab} , v_{cd} are the input and output voltages, and i the current flowing from d through an external circuit, we have for an "ideal" amplifier the relation

$$v_{cd} = Mv_{ab} + R_0 i \quad \dots\dots(1),$$

where M and R_0 are constants characteristic of the amplifier, viz. the voltage amplification factor and the output impedance. In other words, the amplifier is equivalent to a battery or generator of e.m.f. Mv_{ab} and internal resistance R_0 , the equivalent circuit being as in figure 2.

If there is no voltage applied to the input, so that $v_{ab} = 0$, the amplifier behaves with respect to the external circuit connected to cd as a simple resistance of magnitude R_0 . Now let the input and output terminals be connected together, as shown by the dotted line in figure 1, so that $v_{ab} = v_{cd}$. We now have

$$v_{cd} (1 - M) = R_0 i \quad \dots\dots(2),$$

showing that the amplifier now behaves with respect to the external circuit as a simple resistance of magnitude $R_0/(1 - M)$. If we imagine M increased from zero

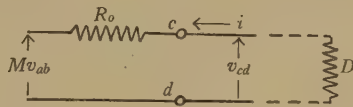


Figure 2. Equivalent circuit of the amplifier.

the value of this resistance will increase from R_0 , becoming infinite when $M = 1$; for $M > 1$ it becomes negative in sign, which means that power is supplied to the external circuit instead of being absorbed from it.

Suppose the external circuit is that shown in figure 1, namely an oscillatory circuit consisting of a coil of inductance L in parallel with a condenser of capacity C . The equivalent series resistance of the circuit at any given frequency being R . Then, as the value of M is increased, the damping of the oscillatory circuit will be reduced, and will become zero when

$$\frac{R_0}{1 - M} = -D \quad \dots\dots(3),$$

where $D = L/CR$ and is the *dynamic resistance* of the circuit at its resonant frequency. This is therefore the condition for the maintenance of oscillations.

This result can also be reached from a slightly different viewpoint, as follows. Consider once more the amplifier in figure 1 without the connexion between c and d but with the oscillatory circuit connected across the output terminals cd . Let a voltage v_{ab} varying sinusoidally at a frequency equal to the resonant frequency of the oscillatory circuit be applied to the input terminals ab . Then it is clear from the equivalent circuit of figure 2 that the output voltage v_{cd} will be equal to $M'v_{ab}$,

$$M' = M \frac{D}{R_0 + D} \quad \dots\dots(4).$$

When $M' = 1$ the source of the input voltage can be removed and c can be connected to d without affecting the oscillations, which then become self-maintaining. The con-

dition for maintenance is thus found by putting $M' = 1$ in equation (4), which then reduces to equation (3).

In the above we have tacitly assumed that a negligible amount of power is consumed at the terminals ab ; in other words, the input impedance of the amplifier is very great. Otherwise, the effect of connecting this impedance across cd must be allowed for. It can easily be shown that the result of connecting a resistance R_1 in parallel with the output terminals of an amplifier is to reduce the effective values of both R_0 and M by the factor $R_1/(R_0 + R_1)$. In the present instance R_1 is the input impedance, and the amended values of R_0 and M should be used in calculating the value of the negative resistance and the condition of maintenance.

§ 3. EFFECT OF AN AMPLIFIER WHICH IS NOT IDEAL

In practice equation (1) will not hold for all values and all modes of variation of the currents and voltages, owing to the effects of inductance and capacity in the amplifier and of non-linearity of the valve characteristics.

Non-linearity of the valve characteristics. If the device is to be used to reduce the damping of a circuit in which forced oscillations are being induced from an external source, the effects of non-linearity can be made as small as desired. It is only necessary to use valves and potentials which are such that the working point does not pass beyond the limits of that part of the characteristic which can be regarded as a straight line. This condition is, of course, that which leads to the absence of wave-form distortion in an ordinary amplifier.

The case of self-generated oscillations is somewhat different. The assumption of a perfectly linear characteristic in this case would be an over-simplification. It would imply that if the maintenance condition were exactly satisfied an oscillation of any amplitude whatever once set up in the circuit would be maintained at that amplitude; moreover, the slightest departure from this condition, such as might be caused for instance by a small change in battery voltage, would result in the amplitude either decreasing to zero or increasing indefinitely. In practice, however, we find that a given circuit condition corresponds to a definite amplitude of the oscillation, and that a small change in this condition merely causes the amplitude to change to one of a different value. This can only be explained by taking account of the curvature of the valve characteristics, which makes the circuit constants (i.e. M and R_0 in the case with which we are concerned) dependent upon the amplitude. Thus, at infinitesimal amplitudes the effective resistance of the oscillatory circuit will be slightly negative. Any small oscillation will therefore grow until it attains an amplitude at which the effective resistance is reduced to zero; the amplitude will then remain constant at this value.

The very existence of a stable, finite amplitude of oscillation thus depends upon the non-linearity of the characteristic, and consequently implies some departure, however slight, from a purely sinusoidal wave-form. If it is desired to keep the wave-form as pure as possible, an oscillator should be operated at a point only just beyond that at which oscillations commence. To enable this to be done it is essential

have some means of control which can produce a gradual and continuous variation of the negative-resistance effect. In the circuit described below this takes the form of a potential-divider controlling the value of the amplification M .

Inductance and capacity in the amplifier. In the case of approximately sinusoidal oscillations we can represent the behaviour of the amplifier at a particular frequency by assigning complex values to M and R_0 .

As far as R_0 is concerned this effect can usually be represented by a small capacity in parallel with the output terminals; this capacity can be incorporated in the value of C , and need not concern us further.

The effect of a complex value of M , corresponding to a phase-displacement in the amplifier, is to cause a shift of the frequency to a new value at which the oscillatory circuit no longer behaves as a pure resistance. Fortunately, since the phase angle of the impedance of an oscillatory circuit changes very rapidly with frequency near the point of resonance, only a small frequency-shift is required to compensate for quite a large phase-displacement in the amplifier. This can be shown as follows.

If x is the fractional change in frequency from resonance and δ the decrement, the impedance Z of the oscillatory circuit is given by⁽⁴⁾

x, δ
 Z

$$\frac{1}{Z} = \frac{1}{D} \left(1 - j \frac{2\pi x}{\delta} \right) \quad \dots\dots(5).$$

Replacing D by Z in equation (4), putting $M = a (1 - j \tan \phi)$ and inserting the condition $M' = 1$, we find that

a, ϕ

$$x = \frac{\delta}{2\pi} \left(\frac{R_0 + D}{R_0} \right) \tan \phi \quad \dots\dots(6).$$

Normally D will be of the same order of magnitude as R_0 , and δ will be a small fraction, so that the fractional change of frequency will not be appreciable unless the phase displacement ϕ exceeds (say) 45° . If the phase-change is due to stray capacity in a single stage, this means that the oscillator will work satisfactorily at all frequencies below that at which the reactance of this stray capacity becomes equal to the resistance with which it is in parallel.

If the amplifier is to act as nearly as possible as a pure negative resistance over a wide frequency-range, inductive couplings are excluded. In a resistance-coupled amplifier however there is a change in phase of 180° in each stage. The amplification is therefore negative with an odd number of stages and positive with an even number. As far as the magnitude of M is concerned, one stage would be sufficient for all ordinary purposes; but in order to obtain a negative value for the resistance, M must be positive in sign, which makes it necessary to use two stages.

If, however, we were to permit the use of an inductive coupling, this could be made positive or negative as required, and it would become possible to use a single stage. The circuit would then in effect be the ordinary reaction circuit. This illustrates the fact that the distinction between the two classes of circuit is not fundamental.

§ 4. THE DESIGN OF THE OSCILLATOR

In figure 3 is shown a practical circuit for an oscillator based on the principle described above, and intended for use at audio and low radio frequencies. It is derived from a two-valve resistance-capacity-coupled amplifier, the only alterations being the connexion between output and input and the variable potential-divider in the anode circuit of the valve V_1 . This potential-divider enables the amplification, and consequently the value of the negative resistance, to be varied as desired; it is thus in effect the reaction coupling of the oscillator. By placing this control in the anode circuit instead of in one of the grid circuits, the effect of stray capacities at high frequencies is minimized.

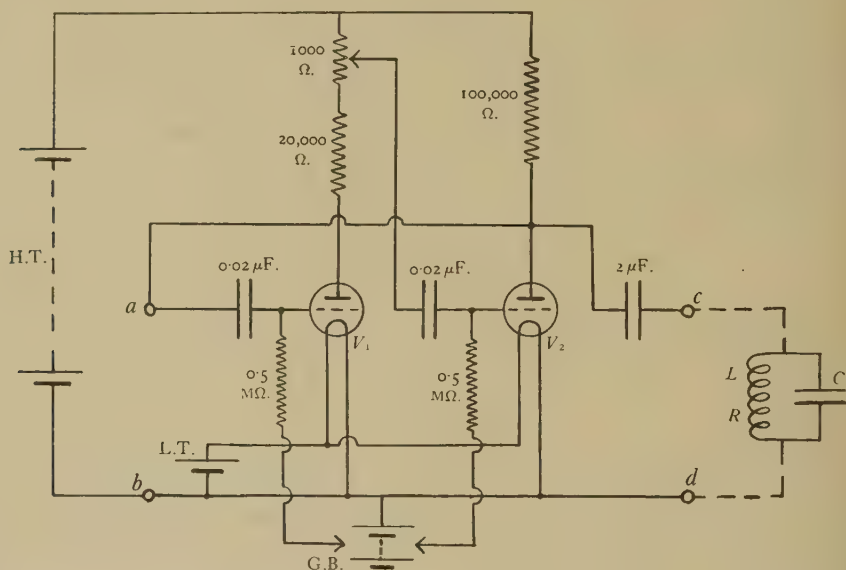


Figure 3. A practical circuit.

As the magnification required is normally much less than the maximum of which a two-stage amplifier is capable, the potential-divider is split into two parts, the variable part having a much lower resistance than the other. The total resistance in the anode circuit is kept high so as to maintain the linearity of the working characteristic of V_1 .

It should be observed that with normal settings of the potential-divider the oscillatory potential on the grid of V_2 will be much less than that on the grid of V_1 . If the valves are at all similar, therefore, the working portion of the characteristic of V_1 may become considerably curved before that of V_2 departs appreciably from a straight line. Thus it is the characteristic of V_1 which determines the amplitude and wave-form of the oscillations; V_2 may be regarded as a linear coupling device, the main function of which is to produce a change in phase of 180° . It follows that the output, for a given harmonic content, will be of the same order as that which would

obtained from the valve V_1 if it were used with the same mean operating potentials in a single-valve oscillator of the ordinary kind. It is of course convenient, though not necessary, to use two valves of the same type. The values of the coupling condensers and grid leaks should be such that their time constants are larger than the period of the slowest oscillations with which it is desired to work.

To ensure satisfactory operation at the higher frequencies the resistances used should have the least possible inductance and capacity. Resistances of metallized or composition type used in wireless receivers are suitable. The usual precautions should be taken to avoid stray capacity effects, especially between the grid and anode circuits of the same valve. It is also advantageous to use valves of low impedance.

If the circuit values given in figure 3 are used, the range over which satisfactory operation is obtained should be from less than 100 c./sec. to something like 500 c./sec. The range can easily be extended to lower frequencies, if desired, by increasing the values of the coupling condensers or grid leaks, or both. The cost of mica condensers becomes high when capacities greater than $0.02\mu\text{F.}$ are required, but if paper condensers are used care must be taken to see that the insulation resistance is maintained.

If the apparatus is required to operate at radio frequencies it is suggested that valves of the h.-f. pentode type should be used, and a screen interposed between the two sets of components associated with the two valves. The 20,000-ohm resistance in the anode circuit of V_1 should be omitted. Such a design should work well at frequencies up to several million cycles per second, and should be nearly if not quite as effective at low frequencies. On the other hand, the valves are more expensive than triodes, and provision would have to be made for applying a suitable voltage to the screening-grids.

The potentials to be applied are those which would be required by the valves if they were used in a normal amplifier. In fact the design requirements can be conveniently summarized by saying that the apparatus will work well as an oscillator or negative-resistance device over the whole range of frequencies and amplitudes for which it would be satisfactory as an amplifier. For most purposes, therefore, the values of the components are not at all critical.

§ 5. EXPERIMENTAL TEST

In order to test the principle experimentally the necessary modifications were made in an existing three-valve resistance-capacity-coupled amplifier, one of the valves being removed. The circuit used was similar to that shown in figure 3, in which the values of the components are given. The main difference was the presence of a decoupling circuit comprising 20,000 ohms and $2\mu\text{F.}$ in the anode circuit of V_2 . Battery valves were used with a l.-t. supply of 2 V. and h.-t. of 200 V. from accumulators. The wave-form of the potential-difference across the terminals cd was observed by means of a cathode-ray oscillograph.

The operation of the device was extremely simple. The biasing potentials were given values which would have been suitable for low-frequency amplification with

the valves in use, and the potential-divider was set for zero amplification. An oscillatory circuit was then connected across cd and the amplification was increased until oscillations just commenced.

Oscillatory circuits of widely different natural frequencies were made up from a miscellaneous collection of inductance coils and condensers. Although some of the coils must have had a high resistance, oscillations were produced in every case without difficulty. By the use of iron-cored coils oscillations were obtained at a frequency judged to be as low as 20 c./sec. The wave-form in this case was bad, but the coupling components were not suitable for so low a frequency (see § 4).

In spite of the fact that the apparatus had been designed as a low-frequency amplifier with wire-wound resistances, no difficulty was found in producing oscillations in a circuit resonating at about 6×10^5 c./sec. corresponding to a wave-length of 500 metres.

Various types of valve were tried, such as the Mullard PM2DX, the Osram HL2, and the Mazda P220. All worked satisfactorily, although their characteristics were very different. It was noticed that V_1 had more effect on the behaviour of the oscillator than V_2 , in agreement with the considerations put forward in the preceding section.

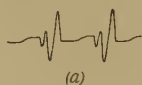
When the amplification was made only just great enough to produce steady oscillation, the wave-form was not distinguishable by eye from a pure sine wave. Any great increase of the amplification beyond this point caused an appreciable increase in amplitude accompanied by a slight change in frequency and by severe distortion of the wave-form, which assumed a shape reminiscent of a typical relaxation oscillation, somewhat similar to that of figure 4 (*b*). This wave-form distortion was particularly marked, even at low amplitudes, when the ratio of capacity to inductance in the oscillatory circuit was small. It must be pointed out that this kind of behaviour is common to all oscillators, and that the circuit described here is superior to most in this respect owing to the range and smoothness of the control.

Production of special wave-forms. As it often happens that a wave-form is required which has a special shape other than that of a sine wave, it may be of interest to record some observations of particular wave-forms and the conditions under which they were obtained. Those chosen for illustration are shown in figures 4, 5, and 6, which are freehand drawings, not to scale, of the oscillograph images. The direction of the time scale is from left to right in each case, and the alphabetical designations are in order of increasing amplification.

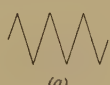
Figure 4 refers to the case in which no external circuit is connected across the terminals cd . The circuit becomes unstable when $M > 1$ and generates relaxation oscillations, i.e. oscillations whose period is determined by the times of charging and discharging of the coupling condensers. Figure 4 (*a*) was obtained when the amplification was only just sufficient to cause instability. When the amplification is very great, as in figure 4 (*c*), the circuit is almost identical with that of the multi-vibrator of Abraham and Bloch, which is used to generate harmonics of high orders for frequency standardization.

Figure 5 illustrates the case when the terminals cd are bridged by a condenser

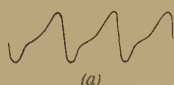
ly. This case is particularly interesting, for when the amplification was only just sufficient to produce oscillations these appeared to be of a purely sinusoidal waveform, although no oscillatory circuit was present. An increase of amplification resulted in a transition to the perfectly triangular form of figure 5 (a), and finally to that of figure 5 (b).



(a)



(a)



(a)



(b)



(b)



(b)



(c)

Figure 4.

Figure 5.

Figure 6.

Figure 4. Wave-forms obtained in the absence of an oscillatory circuit.

Figure 5. Wave-forms obtained with a condenser only.

Figure 6. Wave-forms obtained with an inductance only.

Figure 6 shows wave-forms obtained when a large inductance was connected across cd . When the amplification was great the oscillations took the form of groups of five or six approximately sinusoidal oscillations of equal amplitude, the groups being separated by intervals of quiescence, as shown in figure 6 (b). It is surmised that the period of the individual oscillations corresponded to that of the inductance of the coil in conjunction with its own self-capacity and the stray capacities of the circuit, whereas the period of the groups depended upon the time of charge and discharge of one of the coupling condensers.

6. APPLICATION OF THE INSTRUMENT TO THE MEASUREMENT OF DYNAMIC RESISTANCE.

It is suggested that if the potential-divider controlling the amplification were calibrated, the device could be used to find the dynamic resistance of an oscillatory circuit. The method is as follows. The circuit in question is connected between c and d , and the slider of the potential divider is moved until it reaches the point at which oscillations just commence. Let s be the setting of the slider in this case, i.e. a number proportional to the resistance between the slider and the upper end of the potential-divider. Let s_0 be the value of s which makes M equal to 1; then in general $M = s/s_0$. Therefore from equation (3)

$$D = R_0 \frac{s_0}{s - s_0} \quad \dots\dots(7).$$

R'
 s' To find the value of R_0 , the process is repeated with a known resistance R' connected in parallel with the oscillatory circuit. Let s' be the setting in this case. Then we have

$$\frac{R_0}{D} = \frac{s}{s_0} - 1$$

and

$$R_0 \left(\frac{1}{D} + \frac{1}{R'} \right) = \frac{s'}{s_0} - 1,$$

whence

$$\frac{R_0}{R'} = \frac{s' - s}{s_0} \quad \dots\dots(8).$$

To determine s_0 , that setting is found which just makes the amplifier unstable with no external circuit connected to c and d . Alternatively the values of s' corresponding to two different values of R' can be found, giving two equations of the form of (8) which can be solved for R_0 and s_0 .

This method should be very useful when a number of values of dynamic resistance have to be determined, as for instance in measuring the variation of the dynamic resistance of a circuit with frequency. In such a case R_0 and s_0 can be found once for all, provided the constancy of the batteries and valves can be relied upon.

An endeavour might be made to obtain experimental figures to test the theory given in this section. As the author is not at present in a position to make such an attempt, he publishes the suggestion in the hope that someone with the necessary facilities will find it interesting enough to be worth a trial.

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THE MEASUREMENT OF VERY LOW RELATIVE HUMIDITIES

By A. SIMONS, B.Sc.

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ABSTRACT. Methods available for the measurement of relative humidities lying between 0.5 and 10 per cent are discussed. A dew-point apparatus for measuring dew points down to -40°C . is described, also a hygrometer using wet and dry thermocouples. Calibration curves are given showing the relation between the depression of the wet-bulb temperature and the relative humidity over the above range for air-temperatures between 10°C . and 90°C .

§ 1. INTRODUCTION

IN the course of certain work it became necessary to measure the moisture-content of air which had been dried by means of the usual drying-agents, such as silica gel, calcium chloride or phosphorus pentoxide. The relative humidity of air which has passed slowly over such a drying-agent is very low indeed, ranging from 0 to about 10 per cent, and its measurement presents rather a different problem from those usually encountered in dealing with humidity-measurements.

Many methods are available for the measurement of humidity, but those which seemed most likely to be of practical use in the region in which it was necessary to work were (a) chemical methods, (b) the dew-point method, and (c) the wet-and-dry-thermocouple method. Chemical methods were tried, but the amount of moisture present was so small that accurate determinations by weighing were difficult to carry out. The time taken to make one measurement was such that a continuous record of the dryness of the air could not be obtained. A volumetric form of chemical hygrometer similar to that described by Griffiths⁽¹⁾ has been used successfully for work at low pressures, but is not suitable for use at atmospheric pressure. The dew-point method was tried and a special apparatus was developed by means of which dew points could be measured down to -40°C . Accurate determinations could be carried out with this apparatus, but in making the observations some skill was necessary to detect the first traces of moisture deposited. It was desired, if possible, to develop an instrument which could be made to record continuously with the minimum amount of skilled care and attention. The method which seemed most likely to be of use from this point of view was that using wet and dry thermocouples.

The theory underlying the use of wet and dry thermocouples for the measurement of humidity is well known and need not be gone into here. The problems which arose in using the method in this particular work were due to the fact that the humidity to be measured was so very much lower than any usually encountered. In consequence, the tables which have been drawn up by various investigators

giving the relationship between the depression of the wet-junction temperature and the humidity of the space at any given temperature did not cover the necessary range, which was from about 10 per cent relative humidity down to 0.5 at atmospheric temperatures.

Accordingly a calibration had to be carried out over the required humidity-range for all the temperatures likely to be encountered in practice. This involved the use of some absolute method of measuring the humidity of the space. The only really absolute methods are chemical methods and the dew-point method. The dew-point method was chosen as being simpler and more accurate, but check determinations by means of weighing were carried out from time to time.

§ 2. APPARATUS USED IN CALIBRATION, AND EXPERIMENTAL PROCEDURE

For the purpose of the calibration the apparatus was enclosed in a chamber with a closely fitting glass front so that it could be maintained at any constant humidity. The seal between the chamber and the glass front was made by means of an inflated rubber tube. Heaters, a cooling-coil and a sensitive thermostat were provided so

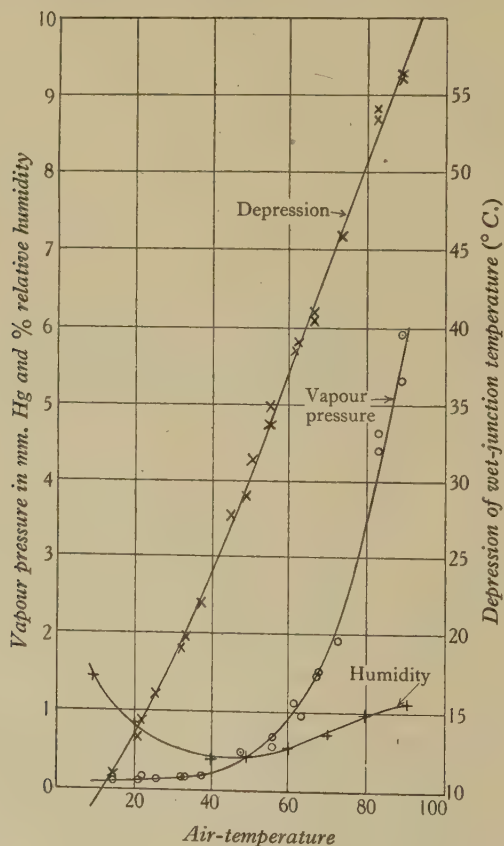


Figure 1. Variation of vapour pressure, relative humidity and depression with temperature.

readings could be taken at any temperature from about 10°C. to 100°C. A tube was fixed to one end of the wet-and-dry-thermocouple apparatus so that a current of air could be drawn through it by means of a fan. The relative humidity was measured by the dew-point method, a mirror being inserted through the top of the chamber. A sampling-tube was provided so that samples of air could be drawn off in order to check the dew-point determinations by actual weighing of the moisture-content of the air. The humidity was controlled by solutions of sulphuric acid in porcelain trays at the bottom of the chamber.

The procedure during calibration was to introduce the sulphuric acid, to close the chamber and then to measure the vapour pressure by means of the dew point method, the depression of the wet couple, after the fan had been left running for some time to enable stable conditions to be reached. The heaters were then switched on, and the thermostat was adjusted to a different temperature and the readings were repeated when the temperature and vapour pressure had again reached equilibrium. This procedure was repeated over the whole range of temperature required. The whole series was then repeated with sulphuric acid solution of a slightly different concentration. The density of the acid used was varied between 1.40 and 1.84 g./cm.^3 , different concentrations being used.

The curves of vapour pressure and depression against temperature were plotted from the experimental readings, figure 1. The values of the vapour pressure at each temperature were read from the curve, and the relative humidity calculated. These values are also shown in figure 1. The corresponding values of relative humidity and depression of wet-couple temperature were thus obtained at each 10° interval over the whole range. From these results curves were plotted showing the relation between relative humidity and the depression of the wet-junction temperature at a fixed temperature. The final smoothed curves are given in figure 6.

§ 3. DEW-POINT APPARATUS USED FOR STANDARDIZATION

The lowest water-vapour pressure which was to be measured was of the order of 1 mm. of mercury at atmospheric temperature. With such a low moisture-content the dew point is about -40°C. and consequently special apparatus had to be devised to reach these low temperatures.

The arrangement finally used is shown in figure 2. A copper rod about $\frac{1}{4}\text{ in.}$ in diameter has a copper disc soldered on to it at one end. The lower end of the rod is turned off on one side for about two inches and polished. This surface is then amalgamated with mercury to serve as the mirror for the detection of dew. A thermocouple is soldered into a hole drilled in the back of the rod so that the junction is just behind the surface of the mirror. A line on the mirror-surface marks the position of the couple. A piece of brass tubing having a copper bottom soldered on serves as a container for a freezing-mixture of solid carbon dioxide and alcohol. The top of the disc on the copper rod and the bottom of the container are ground to ensure good thermal contact. A little alcohol placed on the surfaces prevents the mercury from being lowered by hoar frost.

In taking readings the freezing mixture vessel is placed on top of the mirror stem until dew appears, when the temperature is read by means of the thermocouple. It is then removed and the temperature at which the dew vanishes is noted also.

When the apparatus was first set up a mirror of highly polished stainless steel was used, but it was found that on continued exposure, sometimes at quite high temperatures, in the chamber containing concentrated sulphuric acid, its surface became dulled and the detection of the first traces of dew became correspondingly difficult. Since the steel mirror was very difficult to clean, mercury surfaces were tried and found to be quite satisfactory. These were prepared by polishing the surface with metal polish and then rubbing on a little mercury with the polish and

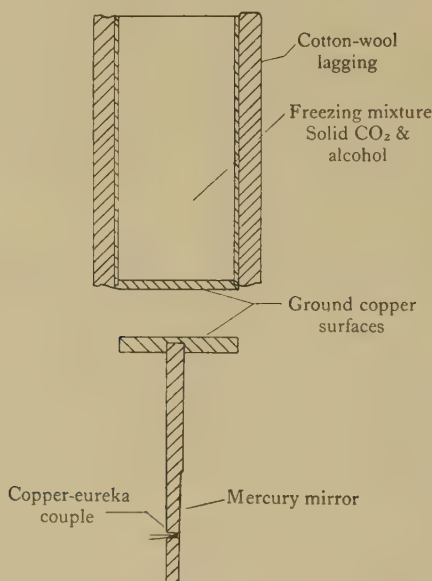


Figure 2. Dew-point apparatus for low temperatures.

finally cleaning with a dry cloth. Although the mirrors required fairly frequent renewal, this was so easy a task that they were used for nearly all the work described here. If the copper surface became badly pitted by mercury it was easily restored by buffing and a new mercury surface was applied.

At vapour pressures above that of water at 0°C ., i.e. 4.58 mm. of mercury, the exact temperatures of appearance and disappearance of the dew were easy to determine. The mist could be watched as it crept down or up the mirror past the spot at which the thermocouple was fixed. Below this vapour pressure, however, the moisture appeared as hoar frost in tiny crystals almost all over the surface of the mirror at once. It was necessary to prevent the mirror from cooling too far past the dew point, or the temperature of disappearance would have been much too high owing to the poor thermal conduction between the frost and the mirror. This could be done by taking a preliminary run to estimate the approximate dew point and

removing the freezing-mixture before this temperature was reached, so that the mirror only cooled down just as far as the dew point. When the mirror was cooled very slowly and closely watched, it was noticed that even at very low temperatures the whole surface of the mirror became misty just at the dew point, though this phase passed almost at once into the crystalline state. The best results were obtained when cooling was arrested just as the frost appeared in the misty stage. To reach the very lowest dew-point temperatures necessary in this work, special care had to be taken to ensure fairly rapid cooling. It was found to be undesirable to lag the copper stem above the mirror on account of the moisture-retaining properties of the lagging. But by regrinding the copper surfaces from time to time and taking care that a layer of oil did not collect on the bottom of the freezing vessel from the carbon dioxide snow, it was possible to reach the lowest temperature necessary. Lower temperatures still could probably be obtained by increasing the diameter of the copper rod.

At the higher humidities the mirror was sometimes found to be cooling too quickly. The rate of cooling could be slowed up, however, by omitting the alcohol between the ground surfaces, or even by placing a thin sheet of paper between them. Alternatively, ice could be used in the pot instead of the usual freezing-mixture.

§ 4. THE WET-AND-DRY-THERMOCOUPLE APPARATUS

The chief difficulties arose from the very large depressions encountered at low humidities. At an air-temperature of 50°C . with a humidity of 1 per cent the depression of the wet junction was about 30°C ., while at the highest air-temperatures depressions of nearly 60°C . were encountered. With depressions of this order conduction of heat to the junction along the wires, along the wick which wets it, and through the air becomes of importance, and unless special precautions are taken the depression for a given humidity and air-temperature will not be so great as that measured by the wet and dry thermometers.

Lanning⁽²⁾ has described an apparatus in which wet and dry thermocouples are used for the measurement of humidity, and he encountered the same difficulty. He allowed for the difference by calibrating the apparatus for sulphuric acid solutions of known density. The aim of the present work has been to reduce the difference to a minimum so that the depression as measured by the thermocouples agrees with that measured by thermometers.

The final form of the wet-and-dry-thermocouple apparatus is shown in figure 3. The depression of the wet-junction temperature was measured by the two couples *A* and *B*, *A* being the dry couple and *B* the wet one. A copper eureka couple *C* was used to measure the air-temperature.

A wick for keeping the wet junction supplied with moisture could not be used, but the junction was wetted by allowing a single drop of distilled water to fall from the capillary tube on to a piece of cotton tied round the couple. To avoid excessive conduction along the wires, very fine wires, 0.0025 in. in diameter, of manganin and eureka were used, copper having too high a thermal conductivity. In order to ensure that the error due to wire conduction had been effectively eliminated, some

samples of exceedingly thin wire 0.0008 in. in diameter were tried. The depressions obtained were, however, identical with those obtained with the wires 0.0025 in. in diameter, and since the latter were much more robust they were used throughout. To keep the temperature of the dry junction steady at the mean air-temperature it was necessary to embed the wires in a fairly large globule of solder. The connexions to the potentiometer from the differential wet and dry couples were made from the

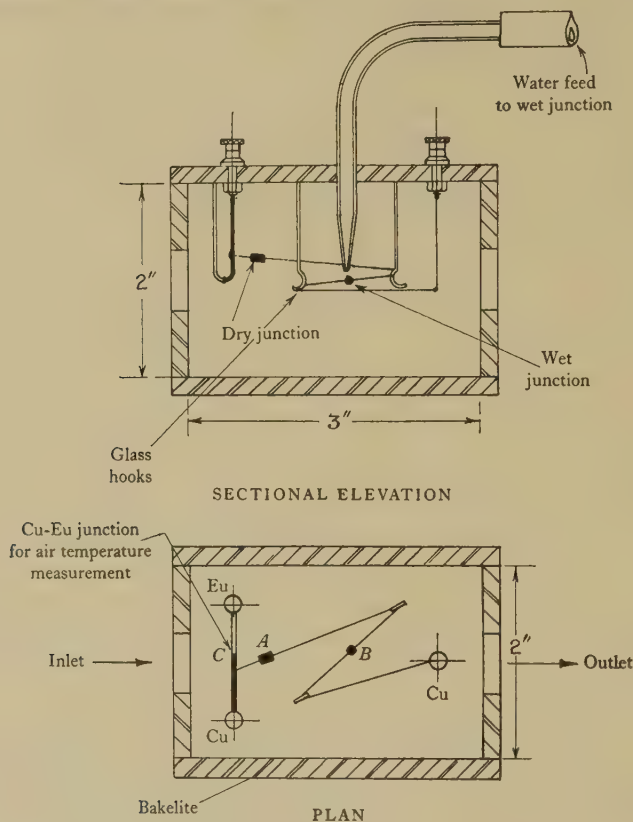


Figure 3. Arrangement of wet and dry thermocouples.

thin manganin wires to fairly thick copper leads to avoid any possibility of errors due to thermal e.m.f.s. at these junctions, the thermal e.m.f. between copper and manganin being very small.

To avoid errors due to thermal conduction through the air it was found that the enclosure in which the couples were suspended must be of a certain minimum size. The necessary distance from the wet junction to the walls of the enclosure was determined by measuring the temperature-gradient through the air around the wet couple by means of a very fine exploring thermojunction. The temperature-gradient is shown in figure 4, from which it will be seen that the distance must be at least 1 cm. to ensure that the temperature-gradient shall not be disturbed by the presence of the walls of the enclosure.

With the apparatus assembled here it was found that the air-velocity past the thermocouple necessary to obtain the maximum depression is very much less than that required in wet-and-dry-bulb thermometer measurements. This is in agreement with results obtained at the National Physical Laboratory⁽³⁾ and by Hilpert⁽⁴⁾. Figure 5 shows the relation between depression and air-flow for a fixed humidity. With the

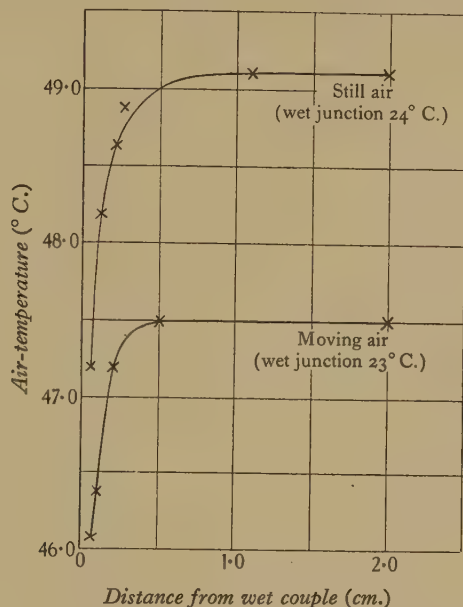


Figure 4. Temperature-gradient in air near wet thermocouple.

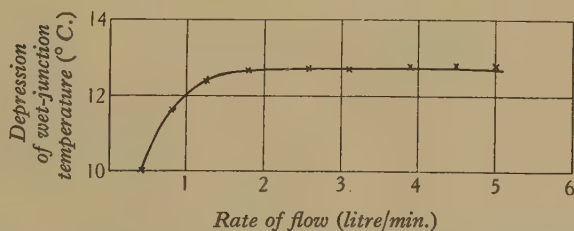


Figure 5. Effect of air flow on depression of wet thermocouple.

of enclosure used, an air-flow of 3 litres per minute was equivalent to an air-velocity of about 2 cm./sec. This gives a great advantage over the wet-and-dry-bulb thermometer, which requires a minimum air-velocity of 3 m./sec., especially when large quantities of gas are being dealt with.

§ 5. DISCUSSION OF RESULTS

The final curves showing the relation between the depression of the wet-junction temperature and the humidity over the range of air-temperatures used are shown in Figure 6. Between 30° C. and 80° C. the results obtained agree very closely with

those given by Griffiths. Above 80° C., however, the depressions given by the wet thermocouples are smaller than those obtained with thermometers. This is probably due to the fact that as the depressions become very large the error due to thermal conduction also increases. The results are plotted in figure 7 together with those of Griffiths. The curves below 30° C. are taken from the Smithsonian tables; they do not agree quite so closely with those obtained in the present work.

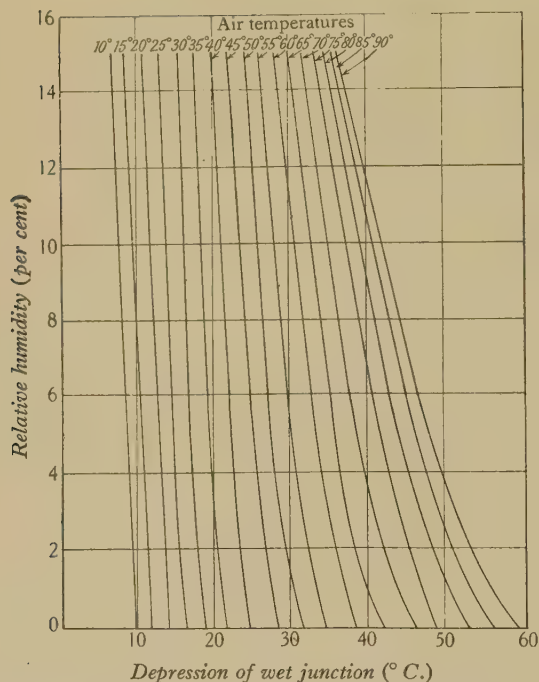


Figure 6. Relation between relative humidity and depression of wet-junction for air-temperatures from 10° C. to 90° C.

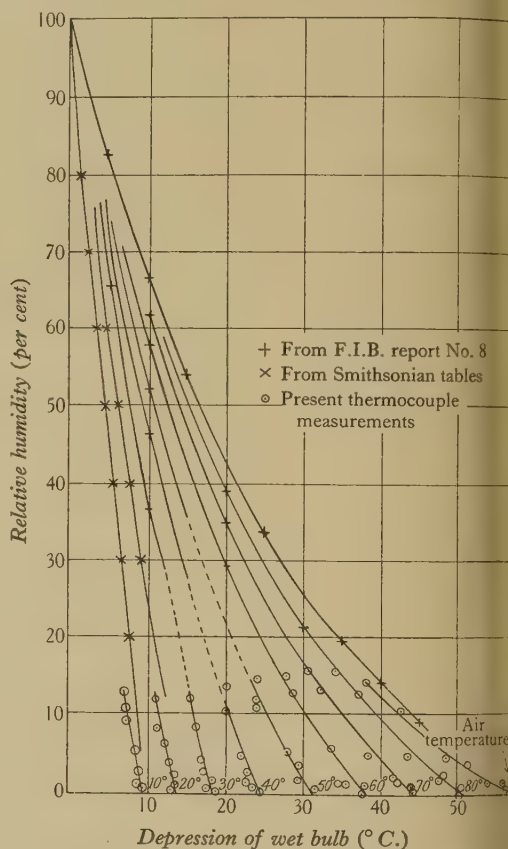


Figure 7. Relation between relative humidity and depression of wet thermometer for various air-temperatures.

The usual formula for the wet-and-dry-bulb hygrometer has been applied to the results as follows:

$$p = pw - AP(t - tw),$$

where p is the pressure of water vapour in the air, pw the saturation vapour pressure of water at the temperature of the wet bulb, t the air-temperature, tw the temperature of the wet bulb, P the atmospheric pressure and A a constant. The value of A was found to be very nearly constant over the temperature-range from 10° C. to 70° C. and equal to 0.00072. From 70° C. to 90° C. the results were not in such close agreement, the value of A increasing for the higher vapour pressures.

A check on the accuracy of the calibrations was provided by the following experiment. The relative humidity of nitrogen from a cylinder was measured in three ways, (a) by absorbing the moisture in phosphorus pentoxide and weighing, (b) by the dew-point method, and (c) by the wet-and-dry-thermocouple apparatus.

The first time that this experiment was attempted the results did not show very good agreement, but this was found to be due to moisture which was given off by the rubber tubing used to connect the various pieces of apparatus to the nitrogen cylinder. When this rubber tubing was replaced by glass connected only by the shortest possible lengths of rubber, very close agreement between the results of the three different methods was obtained.

The weighing experiment was carried out by passing the gas very slowly over two drying tubes in series for several hours, the rate of flow being about 0.5 litre per minute. The rate of flow was measured by a previously calibrated flow-meter. No increase in weight was apparent in the second of the two drying-tubes, and this showed that complete absorption was taking place in the first.

A mercury-mirror dew-point apparatus was fitted up in a vessel so that a current of nitrogen could be passed through it. A pair of wet and dry thermocouples were also arranged so that the gas passed over them after passing through the dew-point instrument.

The results obtained were as follows:

Rate of flow of gas through phosphorus-pentoxide tubes	0.48 litre/min.
Duration of flow	4 hr. 48 min.
Increase in weight of first phosphorus-pentoxide tube ...	0.038 g.
Moisture-content of gas...	0.371 mg./litre.
Air-temperature	19° C.
Density of saturated vapour at 19° C.	16.4 mg./litre.
Relative humidity...	2.26 per cent.
Dew point	-27.3° C.
Air-temperature	19.0° C.
Vapour pressure	0.385 mm.
Saturation vapour pressure at 19° C.	16.5 mm.
Relative humidity...	2.33 per cent.
Depression of wet-junction temperature... ..	13.25° C.
Air-temperature	19.9° C.
Relative humidity from curves...	2.4 per cent.

Thus we have the following values for the relative humidity by three methods:

Chemical method	2.26 per cent.
Dew-point method... ..	2.33 per cent.
Wet-and-dry-thermocouple method	2.40 per cent.

The agreement between these results is sufficiently close for the work for which the apparatus was designed.

§ 6. ACKNOWLEDGMENTS

In conclusion, the author wishes to thank Messrs Callender's Cable and Construction Co. Ltd., in whose Wood Lane Laboratories this work was carried out, for permission to publish it, and Mr A. N. Arman, B.Sc., A.M.I.E.E., for much helpful advice.

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THE EFFECT OF PHASE-CHANGE ON THE COCHLEA

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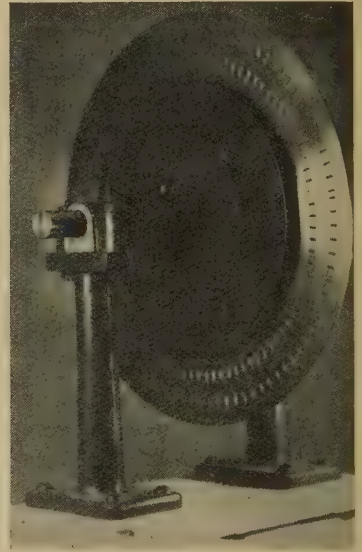
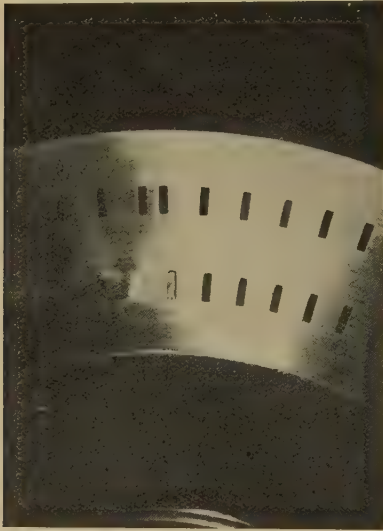
ABSTRACT. A change of phase in a siren tone is produced by means of a special spacing of the slots of the siren. A corresponding interruption of the tone is heard, in accordance with the resonance theory of audition.

SOME years ago I investigated the problem of introducing a sudden change of phase of π (half a wave-length) in a continuous single musical tone. A number of methods were tried without success, because either of noise, or of discontinuity of sound, or of both at the moment of phase-change. The method finally used was to rotate suddenly, through a few degrees, the wind chest of a de la Tour siren during the rotation of the siren disc. Each time this was done the intensity of the tone perceived by the ears was found to suffer a sudden interruption. This experiment is quoted by Beatty⁽¹⁾. He adds "Békésy⁽²⁾, however, repeated the experiment and was unable to detect any silent period". I thought it advisable therefore to repeat the original experiment in a different manner and this was done as follows. A brass disc about 12 inches in diameter was turned truly on a steel shaft. An inner circle of ninety-six equidistant slots was now milled through it from side to side, the distance between the first slot and the ninety-sixth slot being the same as the distance between any other two neighbouring slots. An outer circle of ninety-six equidistant slots was similarly milled through it, the distance between the first and the ninety-sixth slot being only half that between any of the other slots, so that a change of phase of π was thus introduced. When the disc is rotated by an electric motor, and a stream of compressed air through a slot-shaped jet is directed on to the inner circle of slots, a continuous musical tone of constant pitch is produced. When the stream of air is directed on to the outer circle of slots a musical tone of constant pitch is heard, but this tone is interrupted once at each revolution of the disc when the change of phase in the tone occurs. It was found further that the interruption detected by the ears can be imitated by stopping up two neighbouring slots of the inner circle. I concluded that the effect perceived by the ears was a true interruption and not, for example, a change of pitch of the tone. This experiment, therefore, confirmed in every respect my earlier experiment.

It was still possible, however, for the phase-change effect heard originally with the de la Tour siren and now similarly heard with the rotating disc to be due to changes taking place in some structure other than the cochlea of the observer.

Beatty, for example, suggested to me verbally that stationary waves at the walls and ceilings of the laboratory might explain the phenomenon, for when the siren disc is rotating and the musical tone is produced, some of the energy is used to set up and keep going the stationary wave pattern in the laboratory. When the phase is suddenly changed by π this stationary wave pattern would have to be abolished and would have to be replaced by an entirely fresh pattern. Powerful absorption of sound energy would therefore occur and this might be heard by the ear as a break in the sound.

Three experiments, in all of which the attempt has been made to eliminate the possible effects of sound-reflection by the room, have been performed: (i) The experiment has been done in the open air. (ii) The experiment has been repeated



in a sound-absorbing room. (iii) The sound has been conveyed to the ears from the slots in the rotating disc by means of a short length of thick-walled rubber tubing. The open-air experiment (i) was done on a flat asphalt roof far removed from other buildings. A strong wind was blowing. For experiment (ii) the sound-absorbing room was kindly put at my disposal by the General Electric Company. The following particulars of the room have been given me. It was 16 ft. long by 8 ft. high and 10 ft. wide, covered first with two layers of cabot quilt, and completely lined with seven layers of Camgee tissue. The absorption of low-frequency sound energy is believed to be due largely to the diaphragm action of the brown paper confining the eel grass of the cabot quilt, the paper being elastically supported but well damped on either side. In experiment (iii), the rubber pressure tube used was 13 mm. in outside diameter, 6 mm. in bore, and 11 in. in length. One ear was put directly to one end of this tube, the other end being close to the disc on the opposite side to the compressed-air jet.

In each case the effect perceived by the ear was an interruption in the musical tone of the siren each time the change of phase occurred. Further it was found that a similar interruption could be produced by stopping up some neighbouring slots in the inner circle of slots which produced the continuous musical tone. The stopping of one slot produced an interruption that was rather less pronounced, while the stopping of two neighbouring slots produced an interruption that was rather more pronounced than that produced by the change of phase.

The resonance theory of the cochlea depends on two types of experiment for its support, (a) experiments showing that a definite place in the cochlea belongs to tones of a particular pitch and (b) experiments showing that there are resonators somewhere in the ear. With regard to the first type we may mention the recent experiment of Hallpike and Rawdon-Smith, who found that with low-pitched tones the voltage-fluctuations of the action currents were greater near the apex of the cochlea, whereas with high-pitched tones they were greater near its base. With regard to the second type of experiment, it is my opinion that the phase-change effect described in this paper comes in this category, because it is easy to explain the effect if there are resonators in the ear but difficult if there are not. The explanation of the resonator theory is as follows. On change of phase several effects occur: (1) The in-tune resonator comes to rest and then restarts in the new phase. This fall and rise in amplitude should cause an interruption in the tone to be heard. (2) The out-of-tune resonators on the high-frequency side accelerate after the phase-change until they match the new phase. (3) The out-of-tune resonators on the low-frequency side decelerate after the phase-change until they match the new phase. (4) The resonator corresponding to the octave above the musical tone made by the siren receives a slight impulse if the phase-change has been produced by decreasing by half the time interval between the positive phases. (4b) If, however, the phase-change has been produced by increasing by half the time interval between the positive phases, then it will be the resonator corresponding to the major fifth below the musical tone that will receive a slight impulse. (5) Most of the out-of-tune resonators vibrate with small amplitude for a short time after the phase has been changed. This should cause a noise to be heard and the noise should follow the interruption in the tone so closely that the two should be physiologically inseparable. We may say then that on the resonance theory an interruption accompanied by a noise should be perceived by the ears when the phase of a tone is changed

π. The effect on the ear resonators of an actual interruption in a musical tone should be (1) a decrease in amplitude of the in-tune resonator, (2) temporary acceleration of the resonators just above in pitch, (3) temporary deceleration of those just below in pitch, and (4) transient swings of the out-of-tune resonators when the musical tone recommences. The physiological effect to be expected would therefore be a brief interruption in the musical tone accompanied by a noise due to the out-of-tune resonators. Therefore on the resonance theory we should expect a change of phase to produce the same sensation as a short interruption. The experiments described above show that such is the case.

There are many theories rival to that of resonance; one very widely held is the telephone theory. On this theory a change of phase should produce no other effect than the slight sounding of either the octave above or the major fifth below the musical tone suffering the phase-change. Since this is not the effect heard by the ear we conclude that the telephone theory fails to explain the observed phenomenon.

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DISCUSSION

Dr R. T. BEATTY. There is a formidable mass of anatomical and physical evidence that a frequency-analysis of sound takes place in the cochlea, so that there is a one-to-one relationship between pitch and position along the basilar membrane. Such localization of pitch is most plausibly explained by invoking the principles of resonance, and it is for this reason that the resonance theory, though seriously shaken in recent years, still maintains a strong position. The most direct evidence for resonance would be the demonstration of the existence of after-swings, and the author's experiments seem to give a direct proof of their existence.

We must, however, note that a contrary result has been obtained by Békésy,* who excited a telephone by an oscillatory circuit arranged so that by pressing a key the phase of the exciting current changed by 180° . No period of silence was observed. He then placed the telephone in a tuned circuit so as to increase the duration of the transient effect on the diaphragm and observed a silent period when the logarithmic decrement θ per cycle of the tuned system was 0.1. Hence he argues that if θ were equal to 0.1 in the ear resonators the silence should be observable, but as no silence is perceived $\theta \gg 0.1$.

The author states that an interruption was noticed when one slot was closed. If we assume that a 10-per-cent decrease of amplitude of the ear resonator gives a perceptible effect, we have $0.9 = e^{-\theta}$, or $\theta = 0.1$, a value consistent with Békésy's result obtained with a tuned circuit. With this low value of damping we should anticipate a decided effect when the phase is reversed, and this has actually been obtained by Dr Hartridge.

The experiment is of great importance and it is to be hoped that the discrepancy between the work of the two authors will be cleared up.

AUTHOR'S reply. When I originally studied the phase-change effect in 1921 I found great difficulty in producing the phase-change without at the same time producing noises which masked in the ears the beat produced by the phase-change. One of the first methods to be tried was to connect head-phones to a 3-volt 50-cycle alternating current via a spring-actuated two-pole change-over switch which was connected in such a way as to produce a change of phase of half a cycle on release

* *Phys. Z.* **29**, 799 (1928).

the spring. The spring-release was found to be accompanied by a loud click of the telephones which entirely masked any phase-change effect, and this click was reduced but not eliminated by earthing the wire connecting the two magnet bobbins of the telephones. The click is probably due to sudden changes of potential of the telephones, for when the switch contacts break there is a sudden drop in potential, the magnitude of which depends on the point of the cycle at which the break occurs; and when the switch contacts close again there is a sudden rise in potential the magnitude of which depends on the point of the cycle at which closure occurs. Now by chance either breaking or making circuit might coincide with one of the zero-potential points of the a.-c. cycle but it is extremely unlikely that both would do so, and therefore the click is unavoidable and the method a needless one in my hands. I therefore tried other methods of changing phase until finally the de la Tour siren was found to give satisfactory results.* With these satisfactory results obtained with head-phones fresh in my memory I am not surprised that Békésy failed. I should indeed have been very surprised if he had succeeded.

Mr C. N. SMYTH. The author has demonstrated a very interesting experiment, which if sufficiently rigorous will do much to confirm the resonance theory. I feel however that a careful examination needs to be made before it is accepted as conclusive evidence.

The proof of the theory lies in the nature of the silent period to be noticed during the sudden change of phase. Is the short click heard really a silent period, or the production of harmonics external to the ear at the sudden interruption of the note?

To decide this point, electrical methods, and filters, are not conclusive enough, owing in part to the finite mass of the sound-producing mechanisms employed. Could it not, however, be possible to use a siren note of the order of 12,000 c./sec., so that all harmonics would fall outside the audible range? This should be possible with an 8-in. disc and a speed of 3000 r.p.m.; or the services of a top-note deaf observer might reduce the mechanical difficulties. Should the effect not then be noticeable, the magnitude could be increased by having a large number of reversals for every rotation of the siren wheel and listening, under carefully controlled conditions in a damped chamber, for a change in the loudness of the note.

AUTHOR'S reply. The beat ought theoretically to consist of a short silence followed by a short noise. Observation appears to confirm this. It is quite possible that to some observers the silence, and to other observers the noise, appears to be the prominent feature. If the disc be rotated at fast speeds (e.g. 50 revolutions per second) the beat is still there, but at very fast speeds (say 100 rev./sec. or more) its perception fails, possibly because of the short times intervening between repetitions. This difficulty could be avoided by using a siren with a greater number of slots. The present disc is 30 cm. in diameter with 96 slots. If the number were doubled,

* *Brit. J. Psychol.* 12, 142 (1921).

the spacing being the same, the disc would have to be 60 cm. in diameter. The cost of this would be well-nigh prohibitive. If sound film were used it would have to pass the photocell at a speed of about 100 or 200 feet per second. If a gramophone disc were used its speed of rotation would have to be approximately 30-60 rev./sec., so that in each case difficulties, not by any means insurmountable, may be anticipated in attempting to get a tone of 12,000 c./sec.

Dr W. S. STILES. The author has used the term "period of silence" in describing the phase-change effect. I have not had an opportunity of hearing the effect before, and my first impression is of a metallic rap on a background of musical note, with no easily perceptible silent period. In the comparison experiment, which closely simulates the phase-change effect when one or two slots are stopped, it is possible to lengthen the silent period by stopping more slots. I should like to ask the author if there is any marked change in the character of the effect observed as the number of stopped slots is increased.

AUTHOR'S reply. The phase-change causes effects at the ear which closely resemble those produced by a brief interruption in a continuous tone: a silence plus a noise. The cause of the noise has already been elucidated.* A longer interruption produces a relatively larger silence effect and a relatively smaller noise effect.

Mr L. V. K. REIN asked whether the author had given any consideration to the question of bone conduction in connexion with the experiment.

AUTHOR'S reply. The possible effects of bone conduction have been carefully considered. Since the phase-change beat is heard when the sound is led from the siren by a rubber tube to one ear only, the other ear being plugged, and since Banister found that bone conduction of *sound* (in contradistinction to bone conduction of changes of electric potential) is negligible in man, I think it is safe to assume that the phase-change beat does not depend on bone conduction.

Mr J. H. SHANBY. I hope that the author will be able to join forces with Hallpike and Rawdon-Smith at the Middlesex Hospital, present his phase-changed and interrupted sounds at the cat's ear, and observe the results both in the potentials produced on the loud-speaker and after the sounds have been passed through the cat's auditory machinery.

AUTHOR'S reply. Arrangements have already been made for carrying out this suggestion. With Dr Hallpike's and Dr Rawdon-Smith's assistance the wave-form of the siren has been photographed. With a narrow high-velocity jet it is found to be very peaky. With an 8-mm. jet the wave is found to be somewhat flat-topped. With a 5-mm. jet, or better an oval jet measuring 4 mm. \times 6 mm., with its long axis parallel to the long axis of the slots, a very fair sine wave is obtained. When tested on the ear the phase effect is still there and presumably the presence of harmonics is therefore not necessary for the phenomenon.

* Hartridge, *Brit. J. Psychol.* 11, 277 (1921).

Dr J. E. R. CONSTABLE. The fundamental importance of the author's very interesting experiment justifies further attempts to obtain more conclusive results. For instance, an oscillographic study of the note emitted should be made to establish that the short hiss which formed the interruption is not present in the note emitted from the siren. It could, for example, be argued that, as is shown by the photograph of the siren disc, the two phase-changing slots are so near together that there is a position in which air from the jet can pass simultaneously through both. This would produce a short hiss once during each revolution, just as was observed. A test of this explanation could be quickly made by milling a slot midway between two of the slots in the inner circle of equally spaced slots. This, without introducing a phase-change, would make it possible for the air to pass through two slots at once. If the periodic interruption did not then appear, one should feel more sure that the phenomenon was of subjective origin.

If an independent method of producing the phenomenon could be devised it would be of very great value. The author has naturally already tried a number of methods. He mentioned, in particular, that electrical methods are unsatisfactory owing to the clicks caused by switching. There is an additional difficulty about electrical and, indeed, many other methods, namely the fact that they must necessarily involve vibrating systems such as the diaphragm of a telephone receiver. Thus if any phenomena which occur when these methods are used could be accounted for by resonators in the ear they could also be accounted for by the resonant system used for producing the sound. The ambiguity which thus arises could only be dealt with by making measurements of the duration of the interruption.

The possibility of using an electrical method of investigating the phenomena is therefore dependent upon the possibility of designing an electro-acoustic system the phase of which can be reversed in a time which is distinguishably shorter than the two or three periods apparently required by the ear resonators. This requirement would be fulfilled by an aperiodic electro-acoustic system. To be sure of the result, however, it would be necessary to have a more accurate method of estimating the length of the interruption.

The author's observation of the time taken to reverse the phases of the ear resonators also affords a rough method of calculating their sharpness of tuning. The reversal of the phase of the driving force would cause the response of the resonator to fall at first to a minimum value and then to increase again. It would, strictly, take an infinite time to reach its previous amplitude. However, the increase is rapid at the beginning, so that effectively the response returns to its original value in a time which is much the same as that taken for it to reach its minimum. We may take it therefore that the time taken for the response to reach its minimum is of the order of one period of the note. Calculations made on this basis show that the sharpness of tuning of the ear resonators is about 24; i.e. for a note of 500 c./sec. a mistuning of 20 c./sec. would produce a fall in the response of about 3 decibels.

AUTHOR'S reply. With the aid of Dr Hallpike and Dr Rawdon-Smith a cathode-

ray oscillograph record of the note emitted has recently been obtained. With a suitable jet of oval or round section, contrary to expectation, a very fair sine wave-form can be obtained. There is of course some hiss from the siren but it does not appear to affect to any obvious extent the crystal microphone used. I think Dr Constable's point about air passing simultaneously through two jets is met by two variations of the normal procedure: (i) If we use a very small pointed nozzle giving a narrow high-velocity jet of air and place this close to the siren disc the passage of air simultaneously through two neighbouring slots seems very unlikely and yet the phase effect is heard in the normal manner. (ii) The phase can be changed not only by reducing by half a wave-length the distance between groups of slots but also by increasing the distance by half a wave-length. When the latter is done the probability of air passing through neighbouring slots is greatly decreased and yet the phase effect heard by the ear appears to be quite normal. With regard to an independent method of producing the phenomenon I am proposing to try a sound-film record of a tone of constant pitch with the phase-change produced both by cutting a half-wave-length piece out and by putting a half-wave-length piece in. For loud-speaker I propose to use the Duddell sound-producing arc since this is free from diaphragm resonances. When this apparatus has been satisfactorily set up I will ask Dr Constable to come and listen to the resulting phase-change.

If this method proves difficult there is a gramophone-disc method which may be tried as an alternative.

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THE DEPENDENCE OF SENSITIVITY OF THE SELENIUM-SULPHUR RECTIFIER PHOTO- ELECTRIC CELL ON THE OBLIQUITY OF THE INCIDENT LIGHT, AND A METHOD OF COMPENSATION THEREFOR

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ABSTRACT. The paper describes an investigation of the loss of sensitivity of the selenium-sulphur rectifier photoelectric cell with increasing obliquity of the incident light. When a restricted portion only of the surface of the cell is illuminated, it is found that the sensitivity increases as the centroid of the illuminated area is displaced from the centre of the cell. This permits of a simple method of compensation for the fall in sensitivity at oblique incidence, comprising the use of a central stop arranged at a suitable distance above the surface of the cell.

§ 1. INTRODUCTION

THE rectifier photocell can be successfully employed for precise work in illumination photometry only when its sensitivity, defined as the short-circuit current per unit of luminous flux, is independent of the obliquity of the incident light. In any actual cell there is usually a serious loss of sensitivity when the angle of incidence exceeds 70° .

This loss of sensitivity has been observed for many types of marketed cells, and several authors^(1,2,3) have suggested possible methods of compensation. Measurements showing the dependence of the sensitivity for normal incidence upon the position of the centroid of the illuminated area when a restricted portion only of the surface of the cell is illuminated are here described; they prove that the sensitivity increases as the centroid of the illuminated area is displaced from the centre of the cell. This result permits of a method of compensation for the fall in sensitivity at oblique incidence, comprising the use of a central stop in front of the cell.

§ 2. DETAILS OF APPARATUS AND SPECIFICATION OF MEASUREMENT

Cells of the type designated "class A" in an earlier paper⁽⁴⁾ were used for the experimental work. The cell under test was mounted in a holder *AB*, figure 1, and illuminated by a 100-V. 250-W. projector lamp *L*. The lamp was fixed on an arm *c* so that it could be moved round the circumference of a semicircle of radius 100 cm.,

whose centre O coincided with the centre of surface of the cell. When c was normal to AB , the perpendicular to AB through O passed through the light-centre of the lamp, the plane of the filament being parallel to the plane of AB . A telescope was used in the adjustment of the lamp filament. The dimensions of the filament were such that at a distance of 100 cm. the lamp could with sufficient accuracy be re-

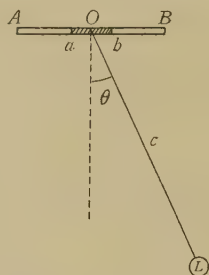


Figure 1. Diagrammatic representation of disposition of apparatus for measuring the distribution curve of sensitivity of a rectifier photocell.

garded as a point source. Moreover, since the maximum radius of the circular plane surfaces mounted in the holder was only 2.5 cm., and therefore small in comparison with the distance of the source, the illumination could be considered to be sufficiently uniform over the surface for the cosine law to apply.

The lamp was operated at 90 volts and gave a candle-power of 282 candles at a colour temperature of 2765° K.; the maximum illumination produced at the cell was, therefore, 282 metre-candles or 26.2 foot-candles. For the range 0 to 26.2 ft.-can. the following relation⁽⁴⁾ holds between short-circuit current, i_e , and illumination E ,

$$i_e = aE - bE^2 \quad \dots\dots(1),$$

where a and b are constants. If I denotes the candle-power of the source, and d the radius of the semicircle, the illumination E at the surface of the cell for any angle of incidence, θ , is given by

$$E = (I \cos \theta) / d^2.$$

Thus if the sensitivity is assumed to be independent of the obliquity of the incident light, equation (1) will give for the short-circuit current i_0 at normal incidence:

$$i_0 = \frac{aI}{d^2} \left\{ 1 - \frac{b}{a} \cdot \frac{I}{d^2} \right\};$$

and at any other angle of incidence θ the short-circuit current i_θ will be given by

$$i_\theta = \frac{aI \cos \theta}{d^2} \left\{ 1 - \frac{b}{a} \cdot \frac{I \cos \theta}{d^2} \right\}.$$

Since terms involving higher powers of the quotient b/a may with sufficient accuracy be neglected, these equations combine to give

$$\frac{i_\theta}{\cos \theta} = i_0 \left\{ 1 + \frac{b}{a} \cdot \frac{I}{d^2} (1 - \cos \theta) \right\}.$$

In an actual cell the sensitivity is a function $f(\theta)$ of the obliquity of the incident light, so that we may write

$$\frac{i_{\theta}/\cos \theta}{i_0 \left\{ 1 + \frac{b}{a} \cdot \frac{I}{d^2} (1 - \cos \theta) \right\}} = f(\theta) \quad \dots\dots(2).$$

The curve represented by this equation will be referred to as the *distribution curve* of sensitivity of the cell. The curves given in all the figures are mean-distribution curves for two coplanar quadrants.

§ 3. UNCORRECTED DISTRIBUTION CURVES

Selenium is extremely hygroscopic, and adequate steps must therefore be taken to avoid exposing the selenium-sulphur film to moist air. Also exposure of the sputtered metal to the atmosphere is found to result ultimately in its complete

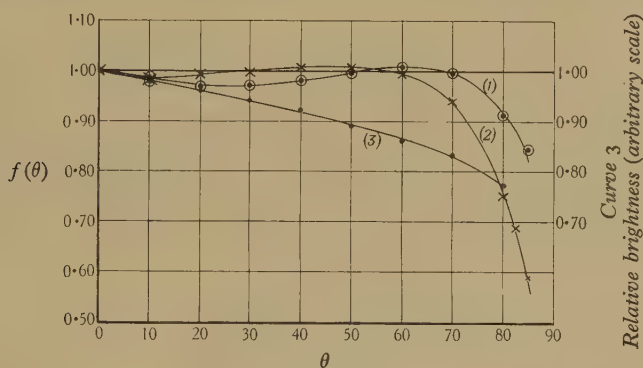


Figure 2. Distribution curves of sensitivity (1) for unlacquered cell and (2) for lacquered cell; and distribution curve (3) of brightness for depolished opal surface with normal view.

integration, metallic aggregates gradually forming and giving rise to electrical discontinuities. A normally sensitive cell may after two months' exposure become almost completely insensitive to light; the cell cannot then be restored to its previous sensitive state.

The cell may be hermetically sealed with a glass window; this method is used in the Weston Photronic cell. It leads, as is shown by the work of Goodwin⁽¹⁾, to an increasingly serious loss of sensitivity with increase in the obliquity of the incident light, owing to loss of light by reflection from the glass window. Alternatively, the cell may be coated with a colourless moisture-proof permanent lacquer; this method has been adopted for the cells produced at the National Physical Laboratory. A lacquer made by the Research Association of British Paint, Colour and Varnish Manufacturers has proved to be satisfactory; it contains cellulose, low-viscosity vinyl acetate, and barkite.

Figure 2 gives distribution curves (1) for an unlacquered cell and (2) for the same cell lacquered. It also gives the brightness-distribution curve (3) for normal view for a ground opal glass test-surface such as is usually employed with a visual

illuminometer. In the case of the unlacquered cell, curve (1), it is seen that the departure from the cosine law is, at any angle of incidence up to 85° , less than that for the depolished opal surface, curve (3); on the other hand, when $\theta > 80^\circ$ the divergence for the lacquered cell, curve (2), becomes increasingly greater than that for the opal. Without correction the lacquered cell cannot be regarded as a satisfactory photoelectric substitute for a visual photometer.

The fall in sensitivity with increasing obliquity of the light may result from (i) loss of light by specular reflection, (ii) dependence of the velocity-distribution of the photoelectrons upon the angle of incidence, or (iii) change in the state of polarization of the light after the light has entered the selenium-sulphur film, giving rise to a change, dependent upon the angle of incidence, in the directional distribution of the liberated electrons. In the case of the lacquered cell, curve (2) shows that much of this decrease in sensitivity is attributable to loss of light by specular reflection. Methods of compensating for this fall in sensitivity will now be considered.

§4. HEMISPHERICAL CELL WITH CIRCULAR APERTURE

At first sight one solution of the problem of compensation would appear to be to form a cell on the inside of a hemispherical shell of metal and to close the hemisphere with a thin opaque disc having a small central circular aperture. From the design shown in figure 3 it is seen that the projected area of the aperture on the

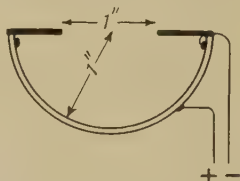


Figure 3. Hemispherical cell with central circular aperture.

surface of the cell is proportional to the cosine of the angle θ between the normal to the plane of the aperture through its centre and the direction of the incident light; hence the incident light-flux is proportional to $\cos \theta$. Further, with the dimensions given in figure 3, light is incident on the hemispherical surface of the cell at an angle not exceeding 30° . Several hemispherical cells were constructed according to this design.

A number of difficulties are involved in the construction of such cells; it is necessary here to mention only two. It is essential first to obtain on the inside of the hemispherical shell a thin and uniform coating of the selenium-sulphur mixture, and for this purpose a polished steel ball very slightly less than two inches in diameter has been used. After annealing, the hemispherical selenium-sulphur film has to be sputtered, and here again the difficulty is to secure a uniform coating. The non-uniform electrostatic field created by the presence of the hemisphere necessitated a modified electrode arrangement, the success of which in producing uniformity of sputtering was confirmed by further results obtained with cells in which

graphite film replaced the sputtered metal film. Uniform and continuous graphite films were obtained by careful polishing with finely powdered Acheson's graphite. A circular Wood's-metal ring around the top of the hemisphere served to make contact with the metal or the graphite film.

The distribution curve given in figure 4 is representative of the results obtained. There is a discontinuity in the curve when $\theta = 52.5^\circ$, since with further increase in the illuminated area on the hemispherical surface increasingly overlaps the ring electrode, so that the response falls off.

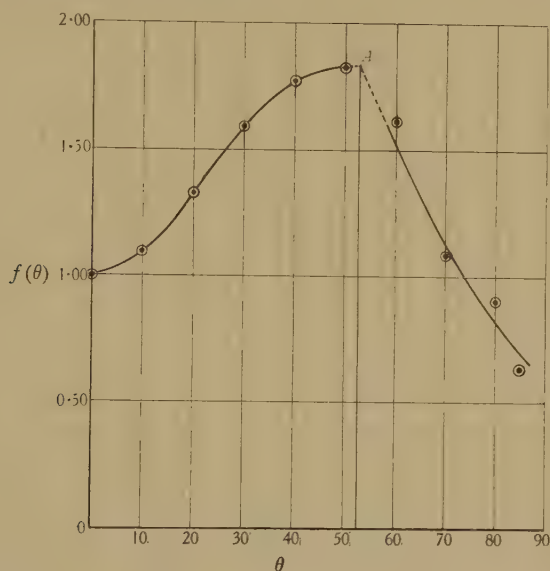


Figure 4. Distribution curve of sensitivity for hemispherical cell with central circular aperture.

The more important part of the curve is that from $\theta = 0$ to $\theta = 52.5^\circ$. It will be shown below that the increase of sensitivity with θ in this region is a consequence of the dependence of the sensitivity upon the position of the centroid of the illuminated area with respect to the circular collecting electrode. This effect renders the hemispherical cell quite useless for the purpose for which it was originally designed.

10. DEPENDENCE OF SENSITIVITY UPON THE AREA OF ILLUMINATION AND UPON THE POSITION OF ITS CENTROID: DISC CELLS

The work on the hemispherical cell indicated that the sensitivity depended either upon the area of illumination, or upon the position of the centroid of the illuminated area with respect to the ring electrode, or upon both. Accordingly, a further investigation of the disc cell was made, and three experiments were carried out. These were confined to circular illuminated areas with light incident normally.

§ 6. DETAILS OF APPARATUS AND EXPERIMENTAL WORK

A holder for an adjustable iris diaphragm was constructed so that it could be mounted vertically on a three-metre photometer bench. The cell under test was mounted on a teak panel which could be easily and accurately moved in a plane parallel with the plane of the diaphragm and 1 cm. behind it. The height of the cell was adjusted so that with a normal view its centre appeared to move along a diameter of the circular aperture. A 1000-W. 100-V. gas-filled projection lamp, operated at 50 V., to give a candle-power of 216.5 candles at a colour temperature of 2360° K., in a known direction perpendicular to the plane of the filament, was set on the bench so that the illumination at the surface of the cell was 10.4 ft.-can., the distance of the lamp filament from the cell being 139 cm. Contact with the sputtered film of the cell was secured by means of an opaque ring of Wood's metal, of inside diameter 3.8 cm. and of outside diameter 4.2 cm., melted centrally on to the selenium-sulphur film before the sputtering to serve as an electrode of the cell.

r_1, r_2
 t Let r_1 denote the radius of the circular illuminated area, r_2 the inside radius of the circular electrode, and t the displacement between the centres of the two circles.

Experiment 1. Various values of t in the range 0 to 1.2 cm. were taken, and at each value of t , r_1 was increased through a range of 0.35 cm., the smallest value possible with the diaphragm available, to $(r_2 - t)$. The sensitivity of the cell was determined at each setting of t and r_1 . The observations show that the sensitivity for any given value of t is independent of the value of r_1 , i.e. of the area of the circular illuminated spot, provided the edge of the illuminated area is not too close to the ring electrode. When r_1 is increased from $(1.7 - t)$ to $(1.9 - t)$, r_2 being equal to 1.9 cm., a slight fall in sensitivity is observed up to a maximum of 5 per cent; but the results obtained for this region are not very consistent. We have therefore the following general empirical result: When the centroid of the illuminated area is fixed, the sensitivity is, for circular illuminated areas, independent of the area of illumination, so long as the edge of the illuminated spot is not very close to the circular electrode.

Experiment 2. With r_1 fixed at 0.35 cm., values of t in the range 0 to 1.2 cm. were taken. At each value of t the illumination at the cell was varied over the range 0 to 17 ft.-can. A curve relating short-circuit current with illumination was thus obtained for each value of t . The observations showed that the deviation from true proportionality between short-circuit current and illumination was the same to within ± 2 per cent for all curves, and therefore that the constants a and b (of equation (1)) are independent of the part of the cell-surface illuminated.

Experiment 3. The lamp was set so that the illumination at the surface of the cell was 10.4 ft.-can., and the following values of r_1 were taken: 0.375, 0.45, 0.55, 0.65 and 0.75 cm. At each value of r_1 , t was varied through the range 0 to $r_2 - r_1$, and the sensitivity was determined for all values of t . The results are plotted in figure 5, which gives the curves relating sensitivity with t for the various values of r_1 . It is seen that the sensitivity is markedly dependent upon the position of the illumi-

d spot with respect to the electrode: the sensitivity increases as the edge of the illuminated area approaches the electrode.

The increase of sensitivity with displacement of the illuminated spot towards ring electrode is doubtless due to the fall in electric resistance of the path of the electron-current from the illuminated area to the ring electrode along the homogeneous and uniform sputtered film.

With the smallest value of r_1 , t was increased beyond $r_2 - r_1$; the illuminated area on the selenium-sulphur surface was thereby reduced, since the illuminated spot overlapped the metal ring to an extent given by the formula

$$A = r_1^2 \cos^{-1} \left(\frac{r_2^2 - r_1^2 - t^2}{2r_1 t} \right) - r_2^2 \cos^{-1} \left(\frac{r_2^2 - r_1^2 + t^2}{2r_2 t} \right) + t \sqrt{ \left\{ r_1^2 - \left(\frac{r_2^2 - r_1^2 - t^2}{2t} \right)^2 \right\} } \dots\dots(3).$$

If the incident light-flux is considered to be constant, the apparent sensitivity produced in the ratio of the effective area to the total area of illumination. This is shown for the case where $r_1 = 0.375$ cm. in figure 5.

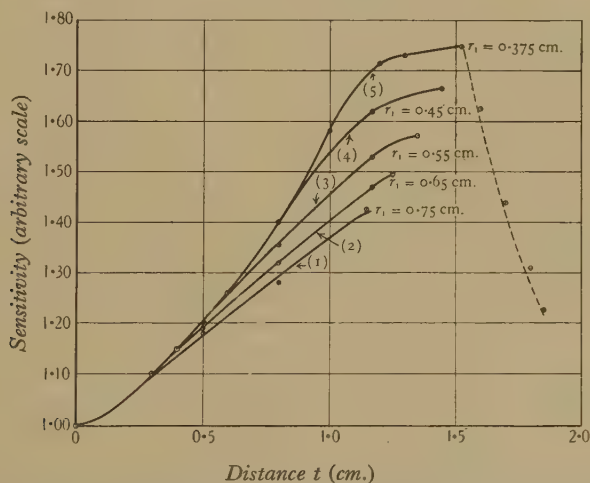


Figure 5. Curve showing the dependence of sensitivity upon the position of the centroid of the circular illuminated spot for various values of r_1 .

The observations made in this experiment give the following general empirical result: When a restricted area only of the surface is illuminated, the sensitivity depends upon the position of the centroid of this area, increasing with the displacement of the centroid from the centre towards the periphery of the cell.

§ 7. DISTRIBUTION CURVES FOR DISC CELLS PROVIDED WITH CENTRAL STOPS

It is seen from figure 5 that advantage may be taken of the increase of sensitivity with t in order to compensate for the loss in sensitivity of the disc cell with increasing inhomogeneity of the incident light, by providing an aperture of suitable radius fixed

centrally at a suitable distance above the surface of the cell. Measurements have been made, with steel and aluminium apertures of various radii, on a number of cells. Representative results are plotted in figures 6 and 7. The correct position of the aperture was determined when the perpendicular to the surface of the cell through its electrical centre passed through the centre of the aperture. The electrical centre was usually at the geometrical centre, but in some cases it appeared to be slightly displaced. At the inside edge of the aperture the thickness of the metal diaphragm was usually made about 0.3 mm. The distance of the aperture from the surface of the cell was measured with a micrometer depth gauge. In figures 6 and 7 the line *C* marks the angle of the incident light at which the edge of the illuminated spot reaches the collecting ring; further increase in obliquity beyond *C* would, of course, result in a large decrease in apparent sensitivity.

With an aperture of radius 0.75 cm., at a distance of 0.75 mm. from the surface of the cell, the deviation of $f(\theta)$, equation (2), from unity is not greater than ± 3 per cent for any value of θ from 0 to 85° , figure 7; with the same aperture at a distance of 0.70 mm. the divergence is not greater than ± 5 per cent for any value of θ from 0 to 87° . These results hold to within ± 2 per cent over a range of illumination of 0 to 25 ft.-can. at normal incidence. It is only necessary to compare figures 6 and 7 with figure 2 to realize the success of this method of compensation in neutralizing the falling away of sensitivity of rectifier photoelectric cells with obliquity of the incident light.

The use of a central stop naturally involves a considerable reduction in the total short-circuit current per foot-candle. For example, a cell of sensitivity $260 \mu\text{A./lumen}$ gives approximately $3.5 \mu\text{A./ft.-can.}$ without the aperture, and only about $0.5 \mu\text{A./ft.-can.}$ with the aperture. A larger aperture is not very satisfactory, as is shown by the results plotted in figure 6. The sensitivity can of course be increased by making larger cells.

§ 8. DISTRIBUTION CURVES FOR DISC CELLS PROVIDED WITH CENTRAL STOPS: COLOURED LIGHT

If the specular reflection factor of the cell-surface is markedly dependent upon the wave-length of the incident light, the distribution curve given in figure 7, curve (2), will only apply for light of colour temperature 2765°K. Actually, however, Pfund⁽⁵⁾ showed that the maximum variation of the reflection factor of an annealed selenium plate throughout the wave-length range 4500 to 7000 Å. was only about 15 per cent of its minimum value. In consequence no very considerable change in the distribution curve is to be expected in the usual range of colour temperature encountered in photometry.

In order to examine this, a holder to carry a standard colour filter was fixed near and in front of the lamp *L* on the arm *c*, figure 1. The lamp was operated at 96 V. at a colour temperature of 2830°K. , and a central stop of radius 0.75 cm. was fixed at a distance of 0.75 mm. from the surface of the cell. The distribution curve was then determined for white light. A colour filter was inserted in the holder, and the

distribution curve redetermined. Distribution curves were obtained with the following colour filters: light green, ortho green, daylight, light orange and light red.

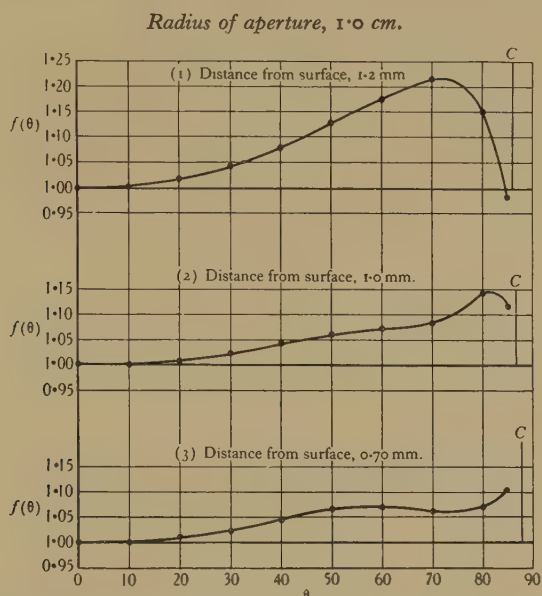


Figure 6. Distribution curves for disc cell with central circular stop.

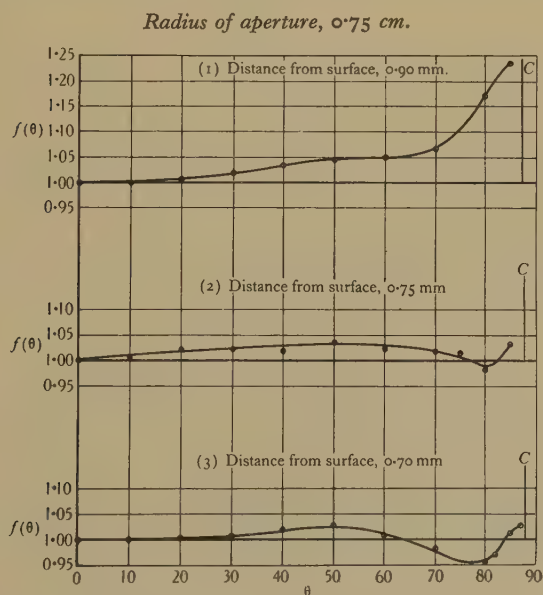


Figure 7. Distribution curves for disc cell with central circular stop.

The quotient of $f(\theta)_c$ for coloured light and $f(\theta)$ for white light is plotted against θ for each filter in figure 8. The results are sufficient to show that with the usual colour-

differences encountered in illumination photometry, the departures from the distribution curve given in figure 7, curve (2), are unlikely to be greater than ± 10 per cent, and in most cases would be much less than this.

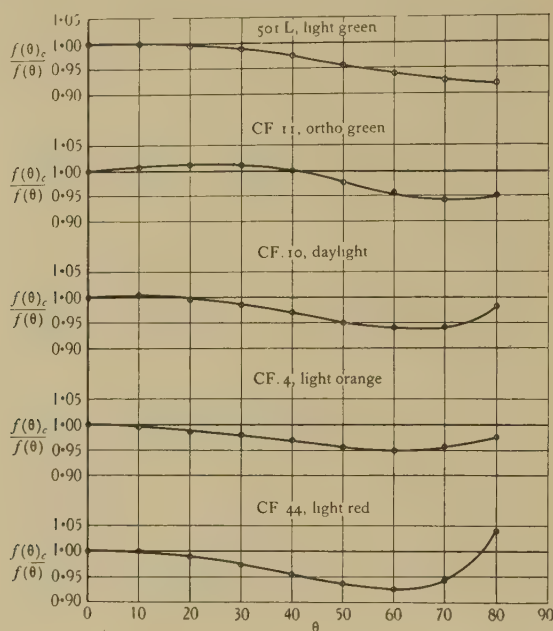


Figure 8. Distribution curves for coloured light: $f(\theta)_\epsilon / f(\theta)$ versus θ .

§ 9. ACKNOWLEDGMENTS

The author is indebted to Mr C. J. W. Grieveson, B.Sc., M.A., for his assistance in the experiments with the iris diaphragm; to Mr C. Dunbar, M.Sc., for his assistance with the distribution curve apparatus; and to Dr G. F. New, of the Paint Research Station, for the cellulose lacquer. He also wishes to record his sincere thanks for the kind interest and constructive criticisms of Dr J. W. T. Walsh and Dr D. Owen.

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DISCUSSION

Prof. L. C. MARTIN asked the author to give particulars of the colour filters used by him.

Dr O. OWEN asked whether results such as those expressed in figure 5 were deducible from any theories of the rectifier cell.

Dr W. D. WRIGHT enquired whether the characteristics shown in figure 5 varied from cell to cell or were common to all cells of a given type.

AUTHOR's reply. The details desired by Prof. Martin are given in figure 9, which gives the spectral transmissions of the colour filters from 4000 to 7500 Å. From these curves, the spectro-photoelectrical sensitivity curve⁽⁴⁾, and the spectral-energy distribution curve of the tungsten-filament source operating at a colour temperature of 2830° K., the effective wave-length and the effective integral transmission ratio of each filter can be calculated.

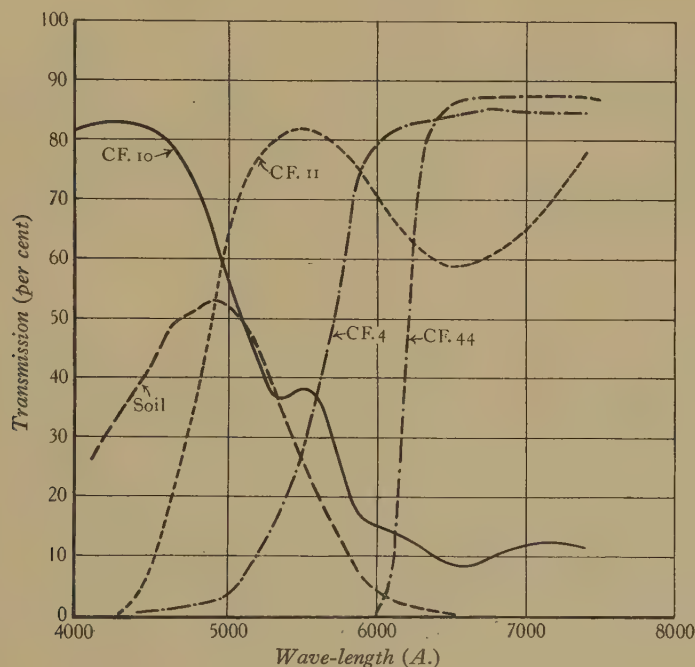


Figure 9. Spectral transmissions of colour filters used to obtain distribution curves for coloured light, figure 8.

I have attempted to find a theoretical explanation of the shape of the curves in figure 5. Strictly, the problem cannot be considered simply as one of conduction in two dimensions. Again, only when t , the displacement, is zero is the distribution of electron-flow along the homogeneous and uniform sputtered film radial. The theoretical investigation is not yet complete, but at present it appears that the available data necessitate a number of simplifying assumptions which would render doubtful the value of any theoretical explanation. I thank Dr Owen for his query.

The curves given in figure 5 are, of course, only valid for the cells described in a previous paper⁽⁴⁾. For cells of the type designated class *A* in that paper, experience has shown that the results hold to within 2-3 per cent.

THE LONGITUDINAL THERMOELECTRIC EFFECT: (6) MERCURY

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ABSTRACT. The Benedicks e.m.f. in mercury contained in an unconstricted glass tube is observed to undergo a reversible decrease with increasing temperatures. The result is in qualitative agreement with previous work. It is suggested that there is an anisotropic quasicrystalline arrangement of the surface molecules of the mercury depending on temperature. Quantitative analysis of the temperature distribution failed to give the homogeneous coefficients, presumably because the effect of temperature on the constants is too marked.

§ 1. INTRODUCTION

THE importance of mercury in the controversy concerning the existence of the Benedicks effect has been realized from the first. Benedicks claimed to have established the existence of the effect in mercury in 1917⁽¹⁾ and published corroborative results in 1919⁽²⁾. During that year, however, Haga and Zernicke⁽³⁾ announced negative results and tried to explain away Benedick's evidence. In 1920 Gouineau⁽⁴⁾ confirmed Benedicks's results again, using mercury in a constricted glass tube. In that year Benedicks himself⁽⁵⁾ reproduced his own original results using constricted tubes of glass, slate and compressed asbestos. In 1921 Bernade⁽⁶⁾ also obtained results using slate containers; he noticed a decrease of the effect with increasing temperature, a phenomenon that was known to Benedicks⁽²⁾, and he was led by this to explain the e.m.f. as due to surface effects between the mercury and the slate container.

The most recent work by Tsutsui⁽⁷⁾ avoids the constricted tube, and immerses the mercury in a uniform capillary glass tube. Tsutsui verified previous positive results, in general, but concluded that the e.m.f. must be due to a molecular or ionic layer constituting the interface between the mercury and glass.

In view of the lack of conclusive agreement, it was thought worth while to check the results for mercury again in the light of methods developed and results obtained here in connexion with other metals.

§ 2. EXPERIMENTAL METHOD

The heating-system was the same as that used in work on silver⁽⁸⁾ to produce asymmetrical temperature-distributions. The mercury was contained in the same glass tube that was used previously to insulate the silver specimen from the brass

thermal shield. Outside the heating-system the glass tube was connected with flexible rubber tubes consisting of bicycle valve tubing; these carried the mercury down to the thermostat where junction with the copper leads was effected. To insure complete circuit within the mercury a T piece was inserted near the heating-system and the mercury-level in this was kept above that in the heater. This open end also served to take up the mercury forced from the heater by thermal expansion during tests.

No satisfactory method could be devised of getting a map of the temperature-distribution in the mercury. All that could be said was that for the same heating-current that was used formerly, the temperature-distribution would be roughly similar with that obtained for wires passing through the glass tube. Since however the mercury represents a greater cross-section of good conducting material than was present in the case of a wire specimen, the temperature-gradients would certainly be less steep. This means that no good analysis of the e.m.f. is possible from the point of view of the theory used in previous papers. It is also difficult to see how we could improve this situation, even by inserting a travelling thermocouple in the body of the mercury: even if the mere mechanical difficulties in the way of such a device were overcome it would still be doubtful whether the thermo-e.m.f. of the couple could be successfully insulated from the mercury circuit.

To get a rough estimate, the effect was tried of inserting wires of greater cross-section, together with the thermocouple in place of the mercury. It was found to decrease the maximum temperature by a few units per cent. We estimate that at least an approximate idea of the maximum temperature can be found for the case of mercury by subtracting 10 per cent from the values previously found for corresponding values of the heating-current. Had the values of the e.m.f. given promise of better analysis, this method of approximation to the temperatures would have been pursued in greater detail. The e.m.f. was measured by the Paschen galvanometer as before, with its sensitivity at $0.094 \mu\text{V./cm.}$

§ 3. RESULTS AND DISCUSSION

In the following table the e.m.f. is recorded against the approximate maximum temperature found as mentioned above. In each case the temperature of the water bath, which was at the lowest point of the temperature-distribution, was near 20°C.

Temperature ($^\circ \text{C.}$)	53	72	95	106	117	130	144	160	175
E.m.f. ($\mu\text{V.}$)	·311	·263	·233	·047	·033	·005	·005	·003	·000

The sudden drop in e.m.f. between 95° and 106° was reversible; in fact in one test the jump of e.m.f. as the temperature dropped was greater than that shown in the above table, which was obtained with progressively increasing temperature.

It will at once be noticed that these results agree, qualitatively, with the positive results obtained before as regards variation with temperature. Further, Benedicks⁽⁵⁾ reported his e.m.f. to be of the order of only $0.035 \mu\text{V.}$ for a temperature-difference of 97.5°C. across the constriction. This temperature-difference corresponds roughly with our maximum temperature 117° in the above table, and the e.m.f.

there recorded is almost identical with that of Benedicks. This agreement must be partly fortuitous because the constriction must have caused quite a different temperature-distribution in Benedicks's case.

A rough temperature-analysis was used in an attempt to find homogeneous constants for correlating the three larger e.m.f.'s. of the above table. No agreement could be found.

This failure is surprising in that mercury is more certainly homogeneous than the other metals in which homogeneous coefficients were found. The most obvious explanation would be that, although the effect is truly homogeneous, the so-called homogeneous coefficients undergo such a rapid decrease with increasing temperature that the methods of analysis here used fail.

However, let us first approach the question in a slightly different manner. Results recently reported for nickel⁽⁹⁾ led us to the suggestion that the homogeneous coefficients were really due to nonisotropic properties of the metal; i.e. to regularity in the arrangement of the microcrystals of the metal. It was pointed out that this view does not contradict the homogeneity theory, but merely supplements that theory.

From this point of view, we are led to enquire what factor in the case of mercury can provide nonisotropic regularity of structure in such a homogeneous substance. Evidently the surface layer of mercury molecules is one possible factor. Langmuir's⁽¹⁰⁾ work on monomolecular films of organic substances in contact with glass suggests at least the possibility of regular molecular arrangements in the surfaces even of liquids like mercury. Direct proof of the existence of highly oriented quasicrystalline structure in the surface of liquid paraffin has been obtained by X-ray diffraction methods⁽¹¹⁾. We can find no references to investigations on these lines concerning mercury, but it seems plausible to assume that liquid crystals would exist in the surface layer. Such a hypothesis would successfully account for the reversibility of the e.m.f. with respect to temperature-variation.

The connexion between surface quasicrystals and surface tension should be intimate. The work of Burdon⁽¹²⁾ on the surface tension of mercury shows a steady decrease of 0.23 dyne per degree up to 230° C.; there is no sudden change near 100° C. corresponding with the sudden change in thermo-e.m.f. observed in the present work. It therefore becomes doubtful if the larger e.m.fs. observed at temperatures below 100° C. can be explained by this surface-crystal theory. It is also doubtful if surface contamination could explain the low-temperature results, because such a hypothesis would hardly be consistent with the good reversibility of the sudden change near 100°.

In fact it seems necessary to postulate the existence within the body of the liquid of quasicrystals whose existence is possible only at temperatures below about 100° C. We hesitate to make this hypothesis because we can find no direct evidence for it in the literature, although the general idea is familiar⁽¹³⁾.

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THE THERMOMAGNETIC PROPERTIES OF NICKEL, PART 2

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ABSTRACT. The homogeneous thermoelectric e.m.f. in nickel is examined for various tensions up to 8 kg. in a pure wire of diameter 1 mm. Analysis gives the new constants (Benedick coefficients) as functions of magnetic field and tension. An antisymmetric part of the e.m.f. with respect to the magnetization has been discovered. Evidence suggesting that the effect is controlled by the regularity (anisotropy) of arrangement of the micro-crystals within the wire is given.

§ 1. APPARATUS

THE heating-system was the identical set used in the work of Pi and Band on nickel⁽¹⁾. The temperature mapping followed the same procedure as that discussed in part 1 of this work⁽²⁾, and in the work of Ch'en and Band on silver⁽³⁾. The e.m.f. was modified to yield greater precision and this change constitutes the chief departure in technique from methods already described in previous communications.

In the first place the e.m.f. found was considerably smaller than that previously obtained for nickel⁽¹⁾, and the sensitivity of the modified potentiometer used in that work was not sufficient. To use the galvanometer method employed in earlier work was felt to be unsatisfactory because it was hoped to make use of the present work in a more precise analysis of the results reported in part 1. The latter were obtained by a potentiometer method in which no current is drawn from the specimen under test and a similar arrangement should therefore be adopted in the present work. The following scheme was adopted after several preliminary experiments with alternative systems.

Figure 1 shows the circuit. A controllable working current is maintained in a resistance box *B* by means of a 2-volt Edison cell and an external rheostat. In parallel with a variable tap in the resistance *B* is connected a standard 10,000-ohm resistance box *S*.* The e.m.f. from the specimen is connected in series with a Paschen galvanometer across the 10-ohm section in *S*, this part of the circuit being provided with a mercury contact switch. All the connexions, the key, and the standard resistance were shielded electrically. The potential-drop across the 10,000 ohms was measured with a K-type potentiometer *K* with the usual accessories.

The procedure thus consists simply of choosing appropriate plugs in the resistance box *B* and a finer adjustment of the rheostat *R* until the Paschen galvano-

* Manufactured by Hartmann and Braun, A.G. Correct to 20° C.

meter indicates zero current through the test wire. The potentiometer K then gives exactly 1000 times the actual e.m.f. required. Since this potentiometer is capable of measuring voltages as small as $0.5\mu\text{V}$, it is theoretically possible to get a quite fantastic order of sensitivity in this way, provided the Paschen galvanometer is adjusted to have a long period. It is found, however, in practice that fluctuations in the controlled working current make it impossible to maintain a balance of such precision long enough to measure it. It is therefore necessary to be satisfied with as low a sensitivity as permissible, in order to avoid such incidental variations. The galvanometer was adjusted with a period of about 2 seconds, and the potentiometer was used in its less sensitive arrangement; final e.m.f. readings were recorded only to $0.01\mu\text{V}$, corresponding to a precision of $10\mu\text{V}$ in the potential-difference directly measured by the potentiometer. Balance could be kept easily enough for this purpose.

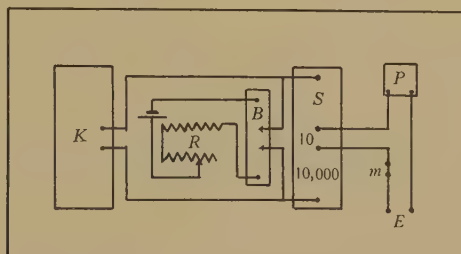


Figure 1. System for measuring e.m.f. K , K-type potentiometer (accessories not shown); R , variable rheostat; B , resistance box, variable tapping; S , standard resistance box, $10,000\ \Omega$; P , Paschen galvanometer; m , mercury contact key; E , e.m.f. under test.

The open-circuit reading of the Paschen galvanometer was found to be independent of stray fields from outside. Reversal of neither the magnetizing field nor heating current caused any detectable change. The mercury switch was provided with a sufficiently long handle for manual operation and treated carefully. It caused slight changes, but only during the first few minutes after initial adjustments. Both poles of the switch were kept at the same temperature by keeping the switch closed most of the time throughout the course of the experiments. It was opened only for momentary tests of the open-circuit zero at each null adjustment.

§ 2. RESULTS

Four temperature-distributions were used, figure 2. They were adjusted to correspond in maximum temperature approximately with the distributions studied in part 1. The integrated values A , equal to $\int (dT/dx) \cdot dT$, and B , equal to $\int (dT/dx)^2 \cdot dT$, for these distributions are given in the following table:

	Temperature map			
	1	2	3	4
$A \times 10^{-3}$	6.7	10.7	11.9	19.3
$B \times 10^{-5}$	5.6	11.5	13.4	27.1

For each temperature the thermomechanical e.m.f. was first found, the combined results being shown in figure 3. There was a slight hysteresis, the return curves lacking the hump in the region between zero and 2-kg. tension, but the final e.m.f. was in each case nearly the same as the initial value. The hysteresis depends upon time, and is evidently connected with elastic recovery after stretching.

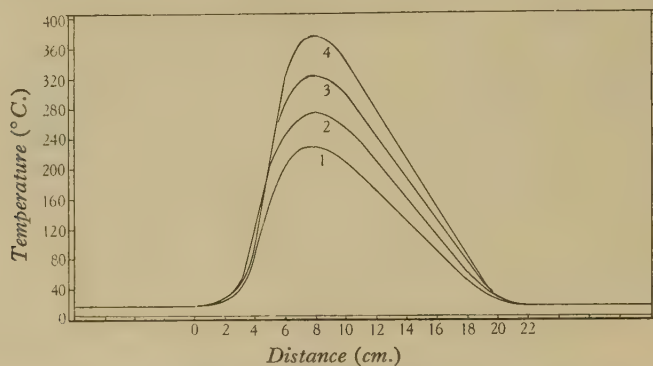


Figure 2. The four temperature maps. (The extent of the centimetre scale coincides with that of the uniform part of the field of the solenoid.)

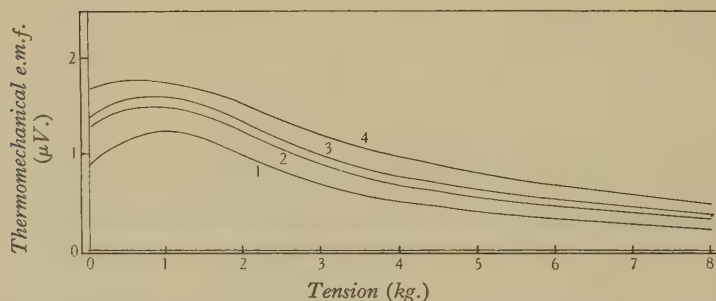


Figure 3. Thermomechanical e.m.f. The numbers refer to the temperature maps of figure 2.

These results were analysed according to the formula

$$E = aA + bB,$$

the method described previously⁽³⁾. It gave the curves for a and b as functions of tension shown in figure 4.

The study of thermomagnetic hysteresis at zero tension was next attempted by means of the hysteresis switching arrangement described in part I. The resulting curve was so complex that it was decided to concentrate attention on the initial rise of e.m.f. with slowly increasing fields before proceeding with hysteresis studies.

This was carried out for both increasing positive and increasing negative fields, where positive field H was directed along AB in figure 2 with respect to the temperature-distribution. Each set of readings was followed by thorough demagnetiza-

on and the initial reading was checked. The results are shown in figure 5. Contrary to expectation the e.m.f. was found to be greatly different for the reversed H , and a special study was therefore made in the region of small fields. Figure 6 shows these results. For values of the magnetizing current* between 0 and ∓ 0.2 A. the e.m.f. is exactly antisymmetrical with respect to the field; outside of this range the curves are entirely different.

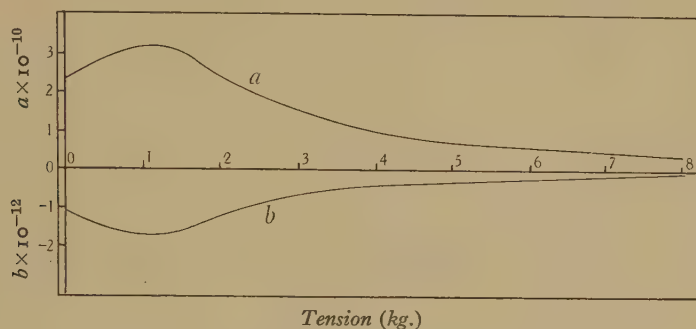


Figure 4. Analysis of the thermomechanical e.m.f.

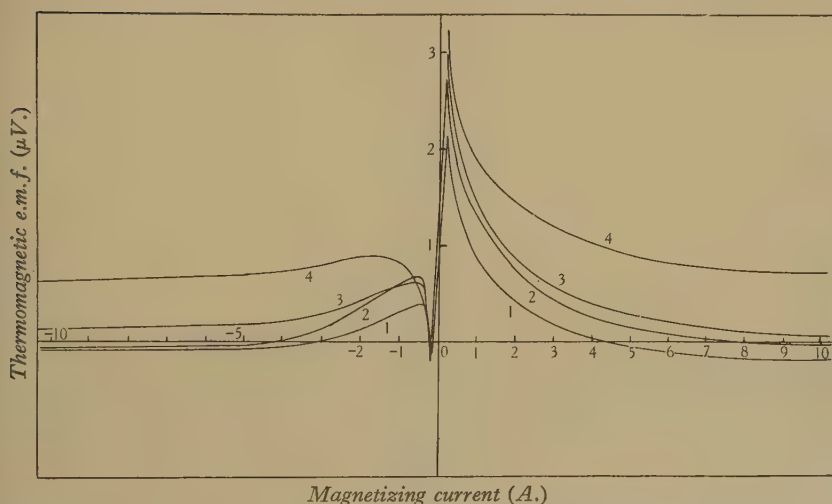


Figure 5. Thermomagnetic e.m.f. Four curves for the four temperature-distributions shown in figure 2. (Zero tension.)

Similar results were obtained for a series of different tensions* up to 8 kg. The values of e.m.f. obtained are summarized in figures 7 to 12. The initial antisymmetry for small fields becomes progressively less with increasing tension.

Analysis of all these data was carried out as before. The resulting values of a and

* A tension of 1 kg. is equivalent to 127 kg./cm² and a magnetizing current of 1 A. gives a magnetic field of 303 gauss.

b lie on smooth curves—see figures 13 and 14. On computation from these values the e.m.fs. are in agreement with observed values to within $0.05\mu\text{V}$.

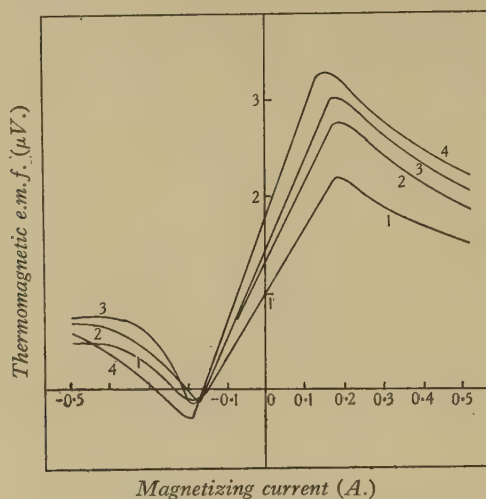


Figure 6. Thermomagnetic e.m.f. Data for a magnetizing field less than 0.5 A.; an enlarged view of the centre part of figure 5. (Zero tension.)

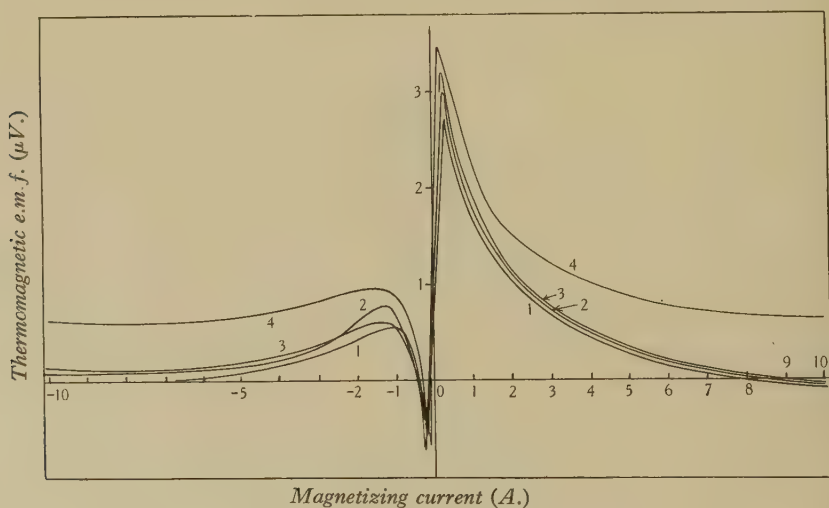


Figure 7. Thermomagnetic e.m.f. with tension 2 kg.

The curves for a can be resolved into symmetrical and antisymmetrical parts by the formulae:

$$a_s = \frac{1}{2} (a^+ + a^-) \text{ symmetrical,}$$

$$a_a = \frac{1}{2} (a^+ - a^-) \text{ antisymmetrical,}$$

where a^+ and a^- mean corresponding values of a for equal positive and negative values of H respectively. The curves for b can be similarly resolved. A plot of a_s

shown in figure 15, reveals some similarity between the behaviour of these symmetrical parts and that of the Thomson potential-gradient inferred from figure 7

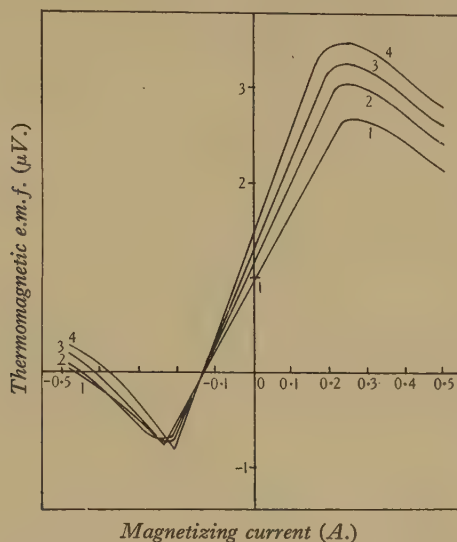


Figure 8. Thermomagnetic e.m.f. with tension 2 kg. An enlarged view of centre part of figure 7.

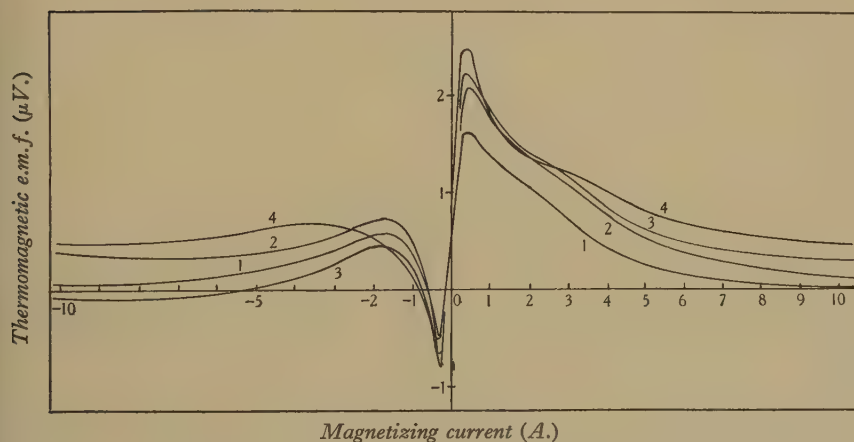


Figure 9. Thermomagnetic e.m.f. with tension 4 kg.

part 1. The antisymmetrical parts shown in figure 16 are quite peculiar, showing, however, a definite critical magnetic field (at a current of 0.2 A.) which is identical with the field at which the sharp minimum in the hysteresis loops was found in part 1.

§ 3. DISCUSSION

Two points call immediately for special discussion. In the first place the values of the e.m.f. and finally the values of a and b here found for nickel are entirely different from those found previously⁽¹⁾. Thus for zero field and a tension of 2 kg. the present work gives

$$a = 2.5 \cdot 10^{-10} \text{ volt-cm./}^\circ \text{C}^2,$$

$$b = -1.4 \cdot 10^{-12} \text{ volt-cm}^2/\text{C}^3,$$

whereas the corresponding result previously found was

$$a = 1.8 \cdot 10^{-9} \text{ volt-cm./}^\circ \text{C}^2,$$

$$b = -1.85 \cdot 10^{-11} \text{ volt-cm}^2/\text{C}^3.$$

The effect of reversing the magnetizing current was not noticed previously, nor was the region for small currents studied. The only essential difference between the two

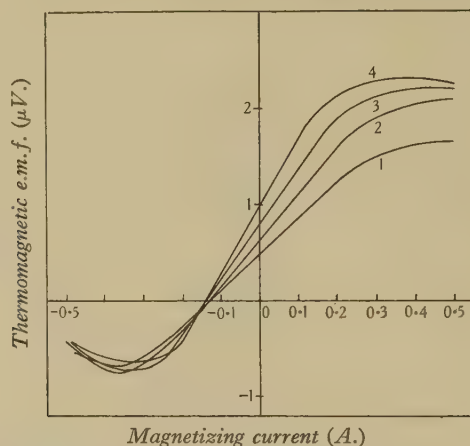


Figure 10. Thermomagnetic e.m.f. with tension 4 kg. An enlarged view of the centre part of figure 9.

samples of wire was in their diameters, which were 0.5 mm. previously and 1.0 mm. in the present work. Both were from the same shipment from Schering-Kahlbaum A.G.

Presumably in the drawing process the final crystalline arrangement will depend considerably upon the diameter. It has been shown by Clark that the drawing process introduces anisotropy in the crystalline arrangement within the wire. These two observations would suggest that perhaps the size and mutual arrangement of the crystals of the metal control the homogeneous coefficients. It should be pointed out, however, that this does not mean that the e.m.f. is not a truly homogeneous effect; the wire must be homogeneous in structure, at least statistically, even though not isotropic. If it were not homogeneous, the analysis used in this work would not succeed: a point which should be clear in the light of results discussed concerning aluminium⁽⁵⁾. However it must be admitted that the constants a and b can no

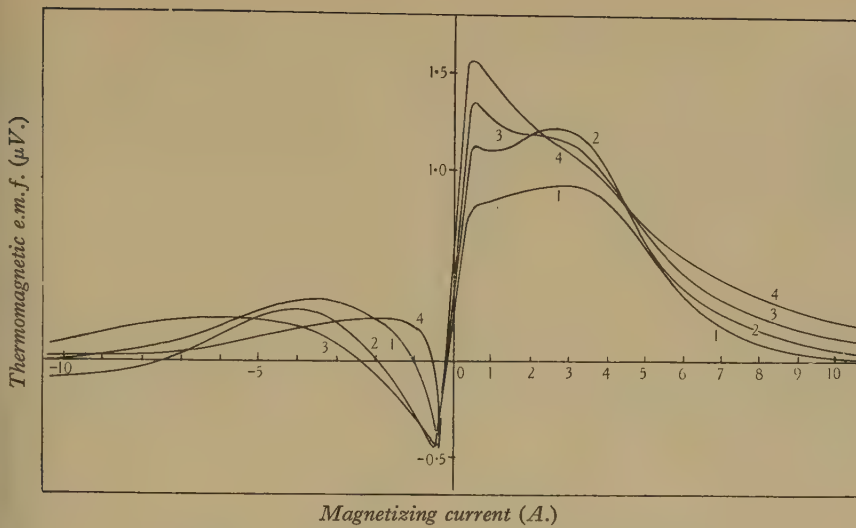


Figure 11. Thermomagnetic e.m.f. with tension 6 kg.

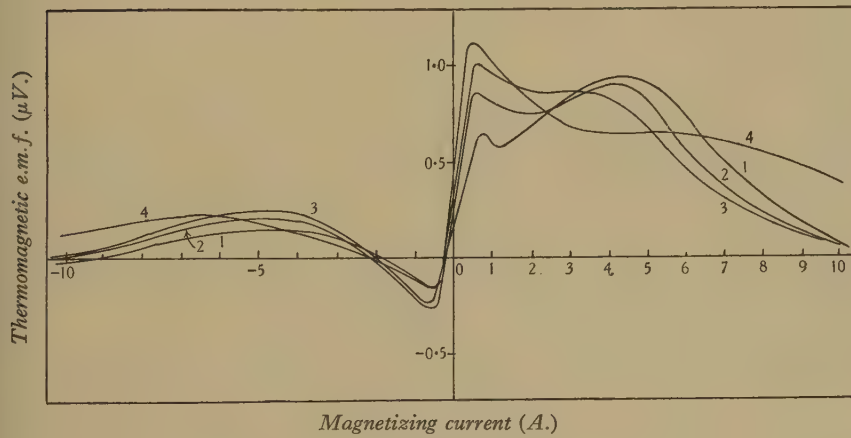


Figure 12. Thermomagnetic e.m.f. with tension 8 kg.

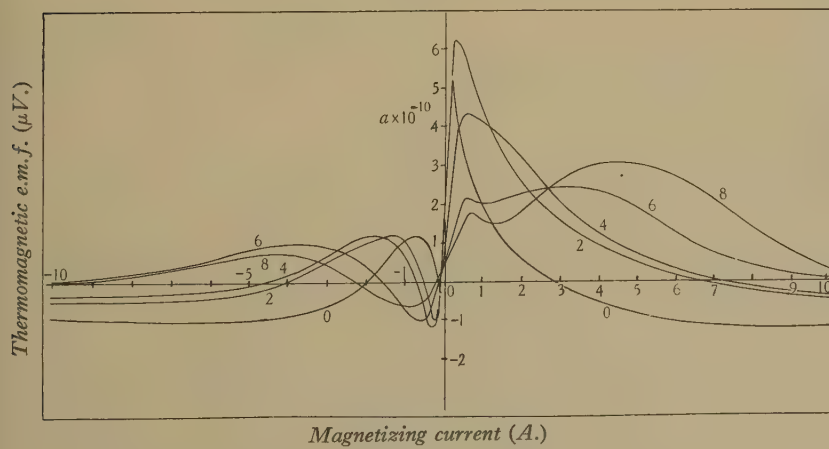


Figure 13. Analysis of thermomagnetic values of a against H for tensions 0, 2, 4, 6 and 8 kg.

longer be regarded as essential properties of the metals themselves; presumably they will depend greatly upon the previous mechanical and thermal treatment of the specimens, if such treatment is sufficient to permanently disturb the crystalline arrangement of the metal.

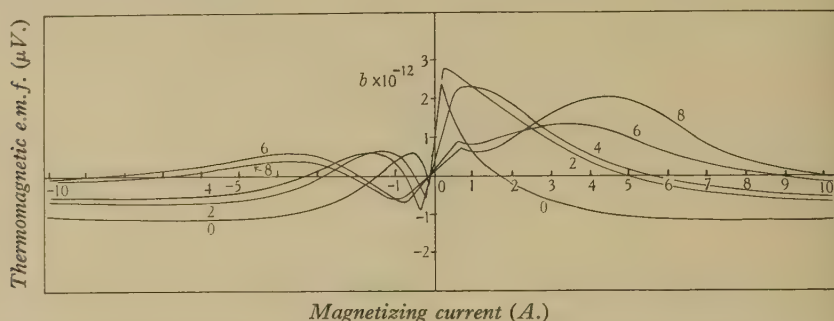


Figure 14. Analysis of thermomagnetic e.m.f. Values of b against H for tensions 0, 2, 4, 6, 8 kg.

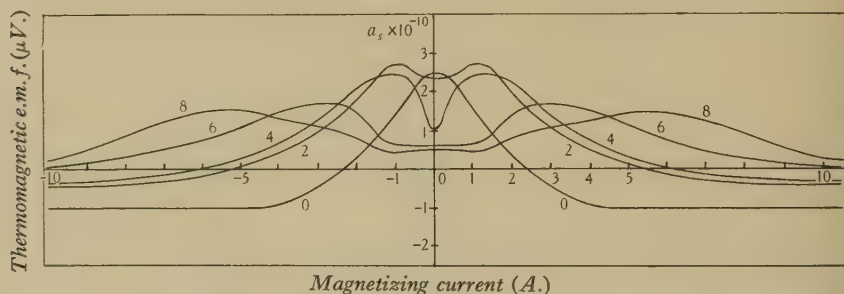


Figure 15. Analysis of thermomagnetic e.m.f. Symmetrical part of a for tensions 0, 2, 4, 6, 8 kg.

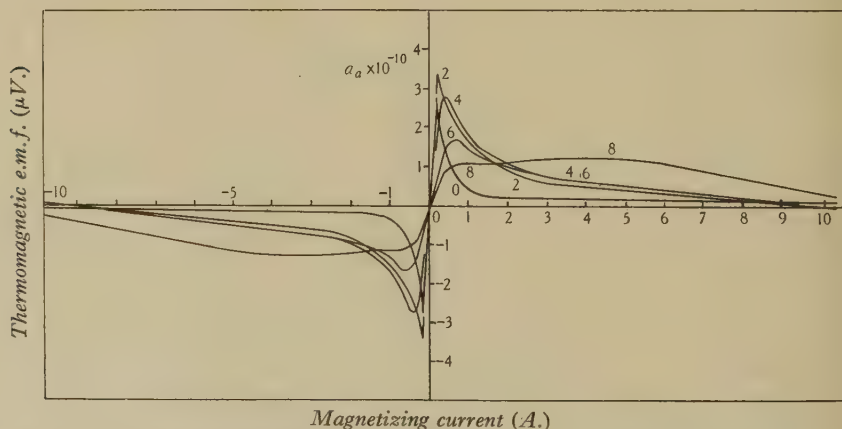


Figure 16. Analysis of thermomagnetic e.m.f. Antisymmetrical part of a for tensions 0, 2, 4, 6, 8 kg.

Since the e.m.f. obtained for the thinner wire was greater than that found for the -1.0 mm. specimen, it would suggest that greater anisotropy produced greater e.m.f. Experiments on single crystals are called for to decide whether this is due to

the integration of elementary effects within the microcrystals or to contact effects at the surfaces between the microcrystals.

In the second place it is natural to seek for some explanation of the quite unexpected form of the curves representing e.m.f. and a and b against magnetizing field. The first suggestions that occur are that (i) some leak from the magnetizing current became connected with the specimen and disturbed the results, or (ii) some variation of the zero position of the galvanometer was caused by the magnetic field. The latter was ruled out by preliminary (and subsequent corroborative) direct tests. The former seems unable to explain the actual form of the antisymmetry of e.m.f. against H ; moreover there is no apparent possibility of mutual contact between the two circuits, as was verified by means of telephone tests. The leak should be directly proportional to the magnetizing current, not merely for small currents, but also for larger values; this is conspicuously not the case for the actual e.m.f. observed.

Further, the genuine nature of the antisymmetrical part of the e.m.f. (and of the constants a , b) is supported by the coincidence between values of magnetizing current, 0.2 A., in this work and in the work of part I where sharp changes in the e.m.f. were observed; the two pieces of work were performed on different specimens of wire from the same roll, in different heating-systems, and with different e.m.f. measuring arrangements.

Speaking in perfectly general terms, we may say that the asymmetrical temperature-distribution, by virtue of the asymmetry, does define a definite sense of direction in the specimen. It is therefore not impossible for the sense or sign of the magnetization also to have some significance when the latter is superposed upon such a temperature-distribution. Up to the present there is no satisfactory physical theory to explain why the thermoelectric force depends upon the temperature-gradient as well as the temperature-difference, although the dependence has been expressed analytically above. We suppose now that the phenomena described in the present paper will have a considerable bearing on the search for such a physical theory.

The correlation of the present results with those of part I is reserved for another communication.

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DUST FIGURES FORMED BY AN ELECTRIC SPARK

BY A. E. BATE, M.Sc., Ph.D., F.Inst.P.

Received June 28, 1935. Read, with demonstration, November 15, 1935

ABSTRACT. The dust figures produced by the sound waves generated by electric sparks passing between a pair of spark gaps in series show interference. Measurements of the patterns made when the distance between the gaps ranged from 15 cm. to 3 cm. show that the wave-length of the sound is constant. When a single spark gap was placed between walls, the sparks produced modified patterns. These are explained by the method of images. The patterns may be regarded as sound maps, and should prove useful in illustrating acoustical phenomena such as the directive properties of cones for high-frequency sound.

§ 1. INTRODUCTION

WHEN an electric spark is passed near a dusty surface the dust is ranged into concentric rings of striae round the spark, the distance between successive rings diminishing as the radii increase. This phenomenon has been the subject of many investigations, among the earliest being those of Mach and Rosicky⁽¹⁾, and among the more recent those of Richmond⁽²⁾, Robinson⁽³⁾, Marsh and Nottage⁽⁴⁾, Campbell and Dye⁽⁵⁾, and Barton and Kilby⁽⁶⁾. The conclusions to be drawn from these papers are as follows: (a) The striae are due to hydrodynamic forces set up by sound waves. (b) The frequency of the sound waves is not necessarily the same as that of the spark. (c) The spacing of the striae varies with the intensity of the disturbance producing them.

The writer repeated the investigation and extended it to the formation of figures by two and three sparks in series, and those formed when a single spark was enclosed between walls.

§ 2. APPARATUS

The apparatus consisted of a coil and condensers for the production of the sparks, spark gaps which could be arranged to give two or three sparks in series, levelling-screws, and plane glass plates, some of which were formed with holes about 1 cm. in diameter to allow a complete pattern to be produced round a vertical spark.

§ 3. PROCEDURE

Single sparks. One of the plates was cleaned, levelled and lightly dusted with dried lycopodium spores which had been sifted to produce uniformity of size. After the lower point of the gap had been set level with the surface of the glass, several sparks were passed through the hole in the plate. As has already been stated, the

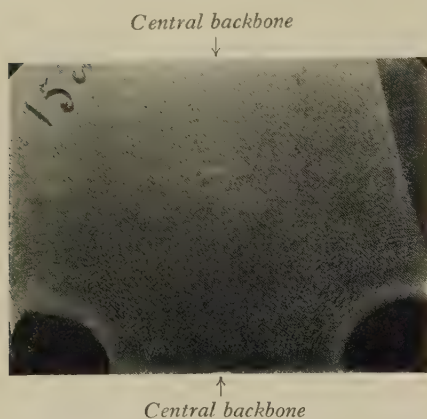


Figure 1. Pattern formed by twin sparks in series, 15 cm. apart.

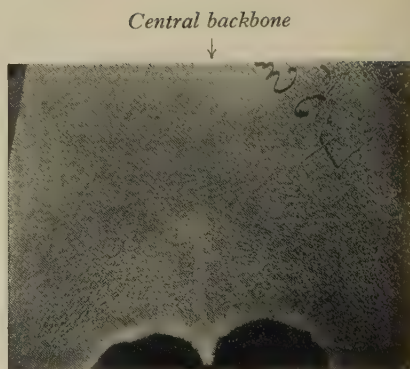


Figure 2. Pattern formed by twin sparks in series, 4.5 cm. apart.

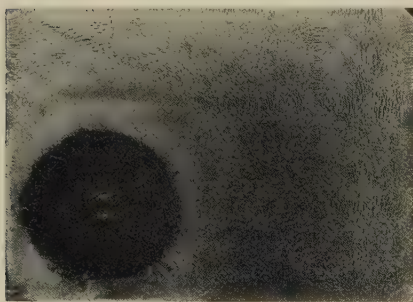


Figure 5(a). Pattern formed in a rectangular enclosure by a spark from a single source.

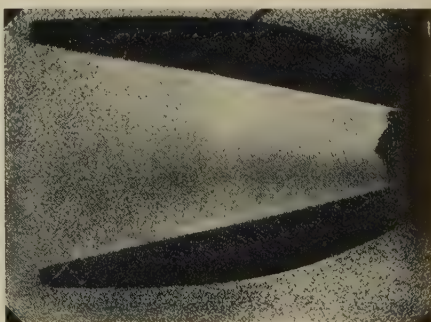


Figure 6. Pattern formed in a horn section (p. 180), spark at narrow end.

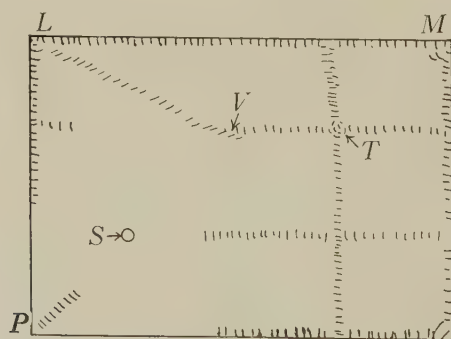


Figure 5(b). Key to figure 5(a) showing main features only.

resulting pattern was made up of concentric rings of powder with the spark as centre. Prolonged sparking only served to accentuate the patterns and to remove the powder from the vicinity of the spark.

Double sparks. Two sparks in series gave patterns which show interference effects, figures 1 and 2. Each of these patterns was produced by sparking under identical conditions except that the sparks were at different distances apart, the positions of the sparks being indicated by the absence of powder. Interference implies the propagation of waves by both sparks.

The striae in the patterns follow a general form. Midway between the sparks and at right-angles to the line joining them is a backbone in which two sets of striae occur. In interpreting these it must be remembered that the resultant effect of the

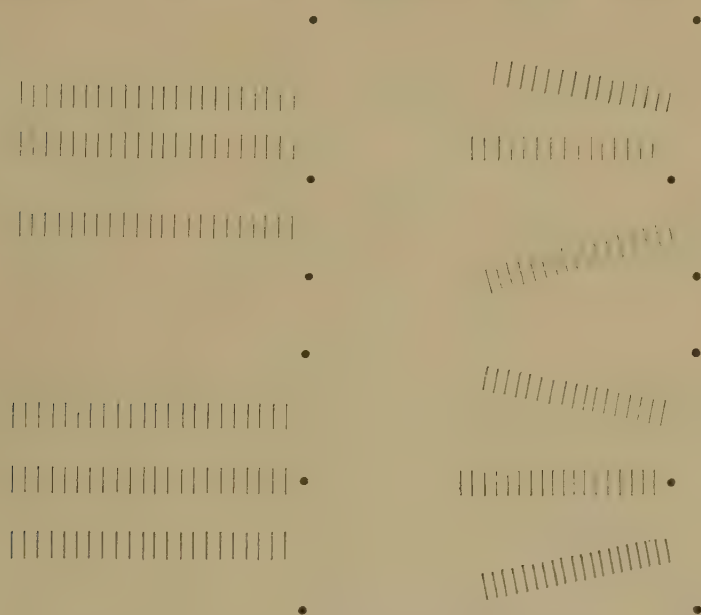


Figure 3. Patterns developed by three sparks in series. Spark gaps are denoted by dots.

spark is at right angles to the direction of the striae. The striae nearer the sparks indicate that standing waves are set up between the latter. Farther out along the backbone the striae are parallel to the line joining the sparks, and thus indicate reinforcement of the waves, which must be progressive. Adjoining the backbone are areas in which the powder is undisturbed, and these are succeeded by areas showing reinforcement. The areas in which the powder is not disturbed are zones* of interference in which the distances of a mean point from each spark differ by half a wave-length. Measurements of patterns in which the sparks were separated by distances varying from 1.5, 3.0, 4.5, ..., up to 15 cm. gave $\lambda = 1.7$ cm.

* When the gaps are close together, the contours of the dust-clear areas show the directions of interference and reinforcement.

These results were obtained on the assumption that the velocity of the sound was constant. Actually the velocity is greater near the spark but falls rapidly to the normal. Foley⁽⁷⁾ found that the velocity of a pulse from an intense spark fell rapidly from 660 m./sec. at 3 mm. from the spark to almost normal at 18 mm., and that the initial velocity varied with the intensity of the spark. The sparks used in the present experiments were less intense than those of Foley, and it is probable that no appreciable error arises in consequence of the assumption that was made.

Three gaps. Three equal gaps in series were next used; their positions and those of the resulting striae are shown diagrammatically in figure 3 for four different arrangements.

All patterns showed the backbone striae midway between each pair of sparks and at right angles to the line joining them.

When the gaps are in line and close together, the adjacent backbones overlap and extend for some distance; this indicates reinforcement in the area at right angles to the line joining the sparks. Maximum reinforcement should occur when the distance between the gaps is half a wave-length, for, as Lord Rayleigh⁽⁸⁾ pointed out, when several sources of sound of the same frequency are in line and are separated by one or an integral number of half-wave-lengths, they project a beam of sound at right angles to the line. Owing, however, to the occurrence of direct sparking between the adjacent gaps when these were close together, the least distance between the sparks that could be used in practice was 1.5 cm.

§ 4. PATTERNS IN CHANNELS

Parallel channels. Two rectangular pieces of wood were placed parallel to each other on a glass plate and the channel between them was sprinkled with lycopodium powder. Several sparks were passed from a single gap placed at the centre of one end of the channel. The resulting pattern showed a central backbone with narrower backbones running along each side of the channel, the striae in the three being ranged at right angles to the channel, figure 6.

When the walls of the channel were close together the striae from the three backbones met to form a single backbone, but when the walls were a few centimetres apart the powder which lay between the backbones was ranged into striae along the channel, and indicated the presence of standing waves. The distance between the walls and the adjacent set of longitudinal striae, being $\lambda/4$, may be used to determine the wave-length.

An interesting pattern was obtained when the spark gap was a centimetre or so from the axis of the channel, for four sets of striae appeared, figure 4(a), one along each wall, the third along a line through the spark gap, and the fourth symmetrically placed with respect to the third. These patterns can be explained by applying the method of images. Let AB and CD , figure 4(b), represent the walls and S the spark gap. Denote primary and secondary images by $S_1, S_1', S_2, S_2', \dots$, the secondary of S_1 being S_2 and so on. Suppose S and S_1 to be isolated sparks; then the resulting backbone striae will lie midway between them, i.e. along AB . Similarly S and S_1' will give rise to the striae along CD , S_2 and S_2' to SX , S_1 and S_1' to TY ;

and it is obvious that the other pairs of images reinforce either of the existing four backbones. When the spark is central, SX and TY coincide.

Inclined channels. If the sides of the channel are not parallel, the four backbones appear, but lie on lines which radiate from the point at which the walls would intersect if produced; two lie along the walls, and the other two are symmetrical, one passing through the spark gap.

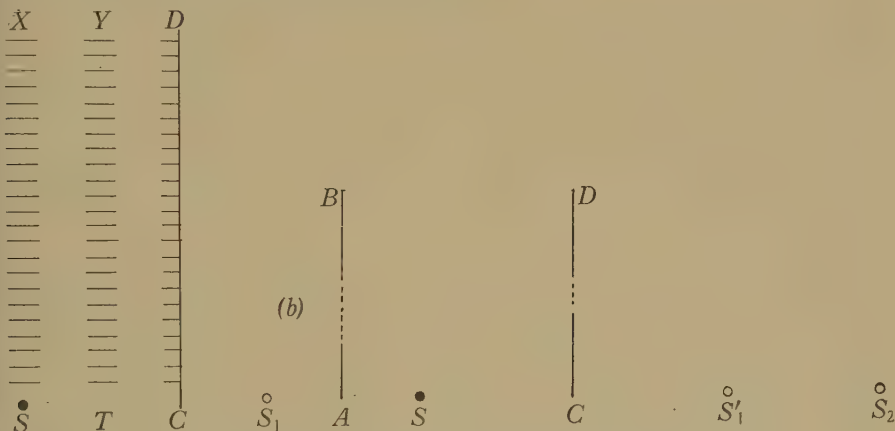


Figure 4. Eccentric spark between parallel walls; (a) main features of striae, (b) mirror images of spark S .

§ 5. PATTERNS IN RECTANGULAR ENCLOSURES

Patterns formed by a series of sparks from a spark gap in a rectangular enclosure show that the parallel-channel effects due to the opposite pairs of sides are superposed, and that these are modified by the inclined-channel effects arising from the adjacent pairs of sides, figure 5(a). Thus the focus at T , figure 5(b), is due to the intersection of the backbone striae, and the inclined backbone LV is due to the inclined sides LM , LP . Finally, the standing waves due to reflection at the walls account for the striae parallel to the walls; these striae coupled with the inclined backbones undoubtedly explain the dimpled appearance of the pattern.

When the walls were covered by a glass ceiling the general form of the patterns remained the same, but the spacing of the striae was modified.

§ 6. SIGNIFICANCE OF THE PATTERNS

These patterns may be regarded as maps of sound, and should be useful in predicting the acoustical properties of an enclosure. If the floor of a three-dimensional scale model of an auditorium be sprinkled with powder and sparks be passed at the point corresponding to the position to be occupied by the speaker or other source of sound, the resulting pattern on the floor is sensibly a map of the sound pattern developed at the level of the ears of an audience. Different wave-lengths may be tested by altering the wave-length of the spark-pulse or by maintaining a constant spark and altering the scale of the model. The effect of draping may be simulated by attaching felt to the model.

§ 7. HORN SECTION

The method was used to trace the path of sound along the section of a horn with curved sides and a curved axis. Two small blocks were shaped to resemble the sections of the sides of such a horn and were placed on a glass plate at suitable distances apart. After the plate had been sprinkled with powder, sparks were passed at the narrow end of the channel. The experiment was repeated with various distances between the blocks. The patterns thus obtained were found to differ, for when the channel was narrow the striae curved round the bend at right angles to the axis of the section, but when the width of the channel was increased the pattern showed a distinct reflection at the concave bend, which probably indicates the presence of a filtering or resonance effect in a horn of this width for the particular wave-length used. Davis⁽⁹⁾ noticed this in his experiments on a horn section in a ripple tank.

When the axis of a horn is straight, the pattern formed resembles that of the channel with inclined sides in that the central and wall striae are present, but differs from it in that the longitudinal striae are absent, figure 6. It will be seen from the photographs that the wall striae join with the central striae for only a short length of the horn, but that the latter persist for a considerable distance. Thus a large horn projecting a short wave-length has directive properties. This was pointed out by Rayleigh⁽¹⁰⁾ many years ago; he showed that a cone will concentrate a hiss, that is a high-frequency sound, in the direction of its axis for a considerable distance if the diameter of its wide end be large in comparison with half the wave-length of the sound.

Since inclined sides project sound but parallel sides do not, a straight horn of rectangular section with one pair of opposite sides parallel and the other pair inclined will project sound along the axis in a fan-shaped path in a plane at right angles to the triangular sides of the horn. This result also is in accordance with Rayleigh's observations⁽¹¹⁾.

§ 8. ACKNOWLEDGMENTS

The writer wishes to record his appreciation for suggestions and helpful criticism by Dr Marsh, of Battersea Polytechnic, in whose laboratory the major portion of the experimental work was performed.

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DISCUSSION

LORD RAYLEIGH said that it was difficult to understand how a sound like the snap of a spark could have a definite wave-length.

DR W. A. LEYSHON asked whether the frequency of the waves might be determined by a mechanical vibration of some solid part of the apparatus.

DR BRUCE CHALMERS. The author has not mentioned what seems to me the most interesting aspect of his work, that is, the cause of the phenomena which he ascribes to interference. The dust figures cannot be due to the accumulation of dust at either the nodes or the antinodes of stationary-wave systems, since their spacing depends upon the intensity of the disturbance, and so cannot be equal to half wave-length at every part of the figure. Hence the interference phenomena are not due to the interference of trains of waves. The formation of the striae seems rather to be analogous to the formation of the transverse ridges in a resonating Kundt's tube, and is clearly due to the interaction between the moving air and the stationary surface, perhaps by the formation of vortex filaments between which the dust collects. The fact that interference effects are obtained when two such systems are superposed might throw some new light on the dynamics of the formation of the figures.

AUTHOR'S reply. In reply to Lord Rayleigh: This point was raised in the discussion following Marsh and Nottage's paper⁽⁴⁾ and it was there suggested that the sound consists of a short train of waves, perhaps twenty in number. The interference patterns in the present experiments indicate that part of the train is of sufficient amplitude to produce striae, or ripples.

In reply to Dr Leyshon: It is possible that mechanical vibrations are set up in the electrodes, particularly as all the pairs of rods forming the gaps were of the same dimensions. The suggestion will be tested by using rods of different lengths.

In reply to Dr Chalmers: The explanation given in the paper appears to have been misunderstood. The distance between successive ripples is not equal to half wave-length, for the ripples are produced by sparks from a single gap, from which no stationary-wave system would be expected to arise. They are clearly due to the same effect as those in a Kundt's tube. The question of interference arises when two sparks are passed simultaneously, for the backbone which persists midway between the sparks has a narrow zone on each side in which the dust is undisturbed. The backbones indicate reinforcement and the zones indicate interference, the difference between the distances from the sparks to a mid-point in either of the zones being half a wave-length.

I wish to thank Mr Lucas and Dr Bartlett for drawing my attention to a paper by Dr E. H. Cook* which deals with the formation of the concentric rings by sparks from a single gap.

* *Proc. phys. Soc.* 9, 371 (1888).

SOME PRELIMINARY NOTES ON DIFFRACTION GRATINGS

BY F. F. P. BISACRE, O.B.E., M.A., B.Sc.

Received October 4, 1935

ABSTRACT. In § 1 a simple test, using polarized light, for the best setting of a diffraction grating is described. When used under the best conditions for brightness, a grating should show little or no polarizing effect. The reason for this depends upon the fact that the Huygens-Kirchhoff integrals for the electric and magnetic vectors have different cosine factors which have the same value only in the case of ordinary reflection. In § 2 an extension of the Huygens-Kirchhoff integrals bringing in a second approximation is given. This second approximation becomes important if either the radius of curvature is comparable to the wave-length of light or the angle of incidence is very nearly 90° , as it may be in soft X-ray experiments. In § 3 a new curve for the effect of slit-width upon the resolving-power of a spectroscope is given and compared with Schuster's curve also. Schuster's curve is based on the assumption that the slit is filled with incoherent light; the author's, with coherent light. These two curves are probably upper and lower limits. In § 4 a new method of ruling concave gratings, namely radial ruling, is suggested. In this method the diamond is given a uniform chordal displacement, from line to line, as in the present method of ruling, but during its displacement from line to line it is constrained to rotate about an axis parallel to the ruled lines and passing through the centre of curvature of the face of the grating. For the metal concave grating of more than 20,000 lines per inch this method of ruling would do what figuring does for an astronomical mirror, though not to so high an order of accuracy.

§ 1. THE POLARIZING PROPERTY OF DIFFRACTION GRATINGS

IN the study of the radiation reflected from gratings it is usual to use some form of Huygens-Kirchhoff surface or line-integral, for instance, in the two-dimensional problem

$$\int \frac{e^{-i\alpha(R+\rho)}}{\sqrt{(R\rho)}} \cos \hat{R}\hat{n} \cdot ds \approx \frac{\cos \hat{R}\hat{n}_0}{\sqrt{(R_0\rho_0)}} \int e^{-i\alpha(R+\rho)} ds,$$

λ, R, ρ
 $ds, \hat{R}\hat{n}$ where α is $2\pi/\lambda$, R the distance from the line source and ρ the distance from the field point to the element ds , and $\hat{R}\hat{n}$ is the angle between the line R and the normal n at the element ds . The integral is taken over the live parts of the cross section of the grating. This, or an equivalent, integral is used in the literature for calculating both the electric and magnetic vectors. It seems not to have been noticed that a distinction should be made; for the electric vector the cosine factor is $\cos \hat{R}\hat{n}$, while for the magnetic vector it is $\cos \hat{\rho}\hat{n}$.

These quantities are the same only for ordinary reflection ($\hat{R}\hat{n}_0 = \hat{\rho}\hat{n}_0$). The explanation of the polarizing properties of a grating lies here. Rowland has stated that metal gratings of 20,000 or more lines per inch consist wholly of grooves with no

its between them. Such gratings would show little or no polarizing effect if they operated under the best conditions for brightness, so that the sides of the active groove reflected as ordinary mirrors, and $\hat{R}n_0 = \hat{\rho}n_0$. This provides a simple test of the best setting of a grating, for it is very easy to examine the light for polarization.

§ 2. AN EXTENSION OF THE HUYGENS-KIRCHHOFF INTEGRAL

These integrals are first approximations, more or less close, to the exact values. Certain experimental evidence exists suggesting that these integrals may be seriously wrong if very small glancing angles of incidence or reflection are in question, such, for instance, as may arise if a grating is used at very sharp grazing angles. These are the conditions which hold when glass gratings are used for determining the wavelengths of soft X rays. The results differ by a small but unwelcome amount from measurements made with crystals.

A second approximation to the exact solution in terms of integrals of the above type has been calculated by the writer. It turns out that it is obtained by merely introducing a factor into the integrand.

This factor is

$$\left(1 - i \cdot \frac{\sec^3 \hat{R}n}{2\alpha r}\right) \quad \text{for the electric vector,}$$

$$\text{and} \quad \left(1 + i \cdot \frac{\sec^3 \hat{R}n}{2\alpha r}\right) \quad \text{for the magnetic vector,}$$

with the change in the cosine factor to $\cos \hat{\rho}n$ instead of $\cos \hat{R}n$ already mentioned. The symbol r represents the radius of curvature of the contour at the element ds . This factor shows at once the order of the error that may be expected. It may be important if either the radius of curvature is comparable to the wave-length or the angle of incidence is very nearly 90° , as it is in the soft X-ray experiments mentioned. In these circumstances, the situation is only saved if λ/r is a sufficiently small number, and it must be *very* small indeed as $\hat{R}n$ approaches 90° . If, for instance, a tightly ruled glass concave grating is used, reflecting only from the untouched polished glass between the rulings, r is finite, and the error will become important if $\hat{R}n$ is sufficiently near to 90° . If plane gratings are used, the limit is likely to be much closer to 90° since the radius of curvature of the facets is probably much greater. Distortion due to ruling may prevent the facets from being quite flat, so that r is not infinite. The correction may thus be important in experiments on soft X rays with ruled plane or concave gratings, especially if a high accuracy is claimed for the results.

§ 3. THE EFFECT OF SLIT-WIDTH UPON RESOLUTION

It has long been recognized that the theoretical resolution of a grating for monochromatic radiation, namely

$$\lambda/\delta\lambda = rM,$$

where r is the order of the spectrum and M is the number of times, applies only for an infinitely narrow slit.

Actually, for finite slits

$$\lambda/\delta\lambda = rM \times y,$$

y, x

where

$$y = F(x) \quad \text{and} \quad x = 2u\sigma/\lambda,$$

u, σ, λ

$2u$ being the angular aperture of the apparatus, σ the slit-width and λ the wave-length.

Wadsworth published⁽¹⁾ values of y , the "purity factor", in 1897. The papers revealed an alleged optimum slit-width at $x=0.2$, where $y=1.09$. Some years later Schuster⁽²⁾ published another table of values of y . His table showed no optimum slit-width. The paper led to a good deal of discussion at the time.*

Both Wadsworth's and Schuster's calculations were based on the assumption that the slit is filled with a set of completely incoherent Huygens sources of uniform strength. The differences in their tables were due to the differences in the methods of mathematical approximation, and a recalculation by the writer has confirmed Schuster's figures. But there is an alternative limiting assumption—the slit may be filled with a series of completely coherent Huygens sources of uniform strength. Since the disturbance at any point P in the slit, due to any single external point source of radiation, is a continuous function, as to both amplitude and phase, of the position of the point P in the slit, it follows that the same is true for the resultant disturbance due to any number of external point sources acting simultaneously, whether these sources be atomic radiators or sources of any other type. Consequently the phase-changes across the slit must be free from the haphazard discontinuities contemplated in the idea of complete incoherence. Some degree of coherence there must be; the question is, how much? The answer to this question depends upon the distances of the sources from the slit, the size of the slit, and the wave-length. With narrow slits, comparable in width to the wave-length, complete coherence may be closer to the truth than complete incoherence, while for wide slits the opposite may be true. The question arises—are the values of y appreciably different for the two alternative assumptions? The writer has made the necessary calculations and finds that with complete coherence in the slit the resolution is improved for narrow slits, the underlying reason being that the wave-fragment passing through the slit is fringed appreciably with ripples of phase and amplitude. These ripples sharpen the image of the slit and enable two images closer together to be resolved by the Rayleigh rule. These effects disappear as the slit-width increases.

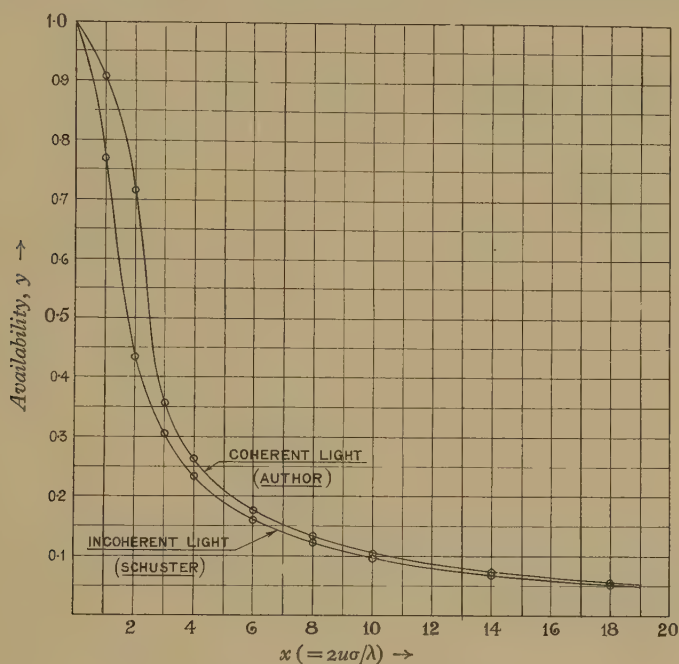
It is just in the case of narrow slits that complete coherence of the light is conceivable for the reasons already given. Probably the truth lies somewhere between these limiting cases—it is a matter for experiment to decide, but suitable experiments have not, apparently, been described. The curves give the results and show that considerable differences in the value of y occur when $1 \leq 2u\sigma/\lambda \leq 3$. In the illustration the word "availability" is used instead of "purity", for this factor shows how much of the theoretical resolution rM is available at any particular value of $2u\sigma/\lambda$.

* See, for instance, reference (3).

§ 4. RADIAL RULING FOR CONCAVE GRATINGS

In the ordinary method of ruling a concave spherical grating, the diamond is given a uniform chordal displacement from line to line as a rigid body. No rotation of the diamond takes place, theoretically at all events.

Suppose, for the moment, that the lines are short enough in comparison with the radius of curvature of the face of the grating, to allow us to consider the surface ruled upon as cylindrical instead of spherical. In these circumstances, the normals to the active sides of the grooves are all parallel, and the width of the active sides of



Effect of slit-width on resolution.

the grooves increases from one side of the grating to the other, for a uniform depth of ruling. Now for optimum brightness, the normal to each active side of a groove should bisect the angle between the lines joining the centre of the groove-side to the slit and the spectral image. The side of the groove will then operate as an ordinary mirror and the total effect at the image will be the cumulative effect of all the active sides of the grooves.

The directions of the normal should, then, change in crossing the grating. Actually, as the grating is ruled, they do not and there is an error in respect of the best direction of the normals. This error is expressible as a power series in θ , the polar angular coordinate of the side of the groove, and the series begins with a first-order term in θ . The first-order term would be completely eliminated if the diamond, during its displacement from line to line, were constrained to rotate about an axis parallel to the ruled lines and passing through the centre of curvature of the face

of the grating; instead of without rotation, as in the usual method of ruling. The truth of this is immediately obvious in the case of a Littrow mounting. Uniform chordal displacement from line to line would, of course, be preserved.

All that is necessary, mechanically, for ruling in this way is to provide a curved guide-way for the diamond-holder instead of the usual straight guide-way. The curvature of the guide-way is the same as the curvature of the face of the grating.

If the grating is ruled in this way, the active sides of the grooves have their normals correctly directed up to errors of the second order, and the lengths of the active sides of the grooves are much more nearly uniform.

If the lines ruled are relatively long, the sphericity of the surface ruled upon will introduce appreciable error in the directions of the normals to the outer groove elements. What has been said above will apply only to the central parts of the sides of the grooves in such cases. Nevertheless, the errors in the outer elements will be considerably less, with this method of radial ruling, than they are with the usual method of ruling.

For the metal concave gratings of more than 20,000 lines per inch, the proposed method of ruling would do what figuring does for an astronomical mirror, though not to so high an order of accuracy.

Preliminary mechanical details of apparatus for carrying out this method of radial ruling have been worked out and the apparatus seems to present no mechanical difficulties greater than those inherent in all ruling-machines. In due course the writer hopes to publish fuller details of all these points.

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THERMOCHEMICAL PROPERTIES OF NITROUS OXIDE

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ABSTRACT. Part I: With a view to determining the heat of formation of nitrous oxide by means of a direct decomposition into its elements, the conditions of initiation and of pressure under which this action will propagate itself progressively and explosively through the gas has been examined. Part II: The heat of formation of nitrous oxide has been directly measured, use being made of this explosive thermal decomposition. The figure obtained is 19.52 ± 0.1 Cal./mol. at constant pressure. Part III: A simple method is given for comparing the values for two gases of the product pressure \times volume, and is applied to the measurement of this product at pressures between 10 and 45 atmospheres in the cases of nitrous oxide and of carbon dioxide.

PART I: THE DECOMPOSITION OF NITROUS OXIDE

By H. R. AMBLER AND T. CARLTON-SUTTON

It has long been known that nitrous oxide can be decomposed by heat, and that a burning body will decompose it progressively if the combustion is sufficiently hot. Berthelot⁽¹⁾ effected the decomposition of nitrous oxide by compressing it very suddenly to 1/500 of its original volume. A less drastically applied compression, however, had little effect, although it was sufficient to initiate the explosion of a mixture of hydrogen and oxygen⁽²⁾. Maquenne⁽³⁾ stated that when 0.1 g. of mercury fulminate was detonated in one atmosphere of nitrous oxide, the gas was decomposed with sufficient violence to shatter the vessel in which it was contained. Houseman⁽⁴⁾ stated that "when under pressure (e.g. in the saturated state) decomposition may be propagated throughout the entire mass of N_2O with explosive violence; if the compressed gas has a temperature above the critical value (38.8° C.) this method of ignition", i.e. ignition by means of heated iron or platinum wire, seldom fails to cause explosion"; exact figures and experimental details were lacking however.

Our experience with this gas was not in accord however with the above statements, and a further investigation was undertaken. This has shown that decomposition is not propagated at pressures below 13 atmospheres but can be propagated at pressures above 13 atmospheres.

When small quantities of lead azide were detonated in atmospheres of nitrous oxide at various pressures, it was found that the proportion of nitrous oxide de-

composed increased rapidly with increase of the initial pressure, and that at the higher pressures the explosion was complete and was an intrinsic property of the nitrous oxide itself. For example, while decomposition does not occur at atmospheric pressure, 10 per cent of the nitrous oxide is decomposed at a pressure of 10 atmospheres and more than 99 per cent is decomposed at pressures above 35 atmospheres.

A simpler method of initiation was found in the fusing of an electrically heated platinum wire. The initiation was not due entirely to the energy supplied to the wire and the temperature attained by it, since the fusion of a wire in a low-voltage, low-resistance circuit of low inductance was not sufficient to cause explosion. Explosion was obtained, however, when the production of a spark on the fusing of the wire was ensured by either (i) the introduction of additional inductance and capacity, or (ii) an increase of the voltage above 20. The initial temperature was approximately 20° C. throughout.

As will be seen from table 1, the pressure which determines whether explosion is propagated lies between 12 and 15 atmospheres.

Table 1

Initial pressure of nitrous oxide (atmos.)	Number of determinations	Nitrous oxide decomposed (per cent)	
		Extreme values	Mean values
2			} < 1
5			
7			
10			
11	3	1·3-7	4
12	3	9-35	23
13	4	0·5-85	41
14	3	66-89	
15	1		88
30	2	91-95	93
37	1		91
42	6	91-93	92
48	1		93

PART II: MEASUREMENT OF THE HEAT OF FORMATION OF NITROUS OXIDE BY DIRECT DECOMPOSITION

By T. CARLTON-SUTTON, H. R. AMBLER AND G. WYN WILLIAMS

§ 1. HISTORICAL

The measurement of the heat of formation of nitrous oxide has become important in recent years on account of its being a datum in the determination of the specific heats of gases at high temperatures. Hitherto the heat of formation has been deduced from measurement of the heat produced when nitrous oxide reacts with

hydrogen or with carbon monoxide. Whichever of these reactions is used, some 80 per cent of the heat measured comes from the oxidation of the combustible gas, the heat of formation of the nitrous oxide contributing the remaining 20 per cent; any error in the thermal measurement will therefore be magnified by about five.

Figures which have been obtained for the heat of formation of nitrous oxide by these combustion methods are given in table 2. The present writers have also used these methods, employing pressures of about 50 atmospheres; the figures which have been obtained and the causes which have made the procedure unsatisfactory at these pressures are discussed in § 4.

Table 2. Determination of heat of formation of nitrous oxide by combustion methods

Observer	Method	Heat of reaction (Cal./mol.) _{cp}	Deduced heat of formation of nitrous oxide (Cal./mol.) _{cp}
Berthelot ⁽⁵⁾	Combustion with CO at constant volume	88.2	-20.6
Thomsen ⁽⁶⁾	Combustion with H ₂ at constant pressure	86.3	-18.01
Thomsen ⁽⁶⁾	Combustion with CO at constant pressure	85.1	-17.47
Awbery and Griffiths ⁽⁷⁾	Combustion with CO at constant pressure	87.1	-19.5
Fenning and Cotton ⁽⁸⁾	Combustion with CO at constant volume; pressure about 5 atm.	87.4	-19.75
Fenning and Cotton ⁽⁸⁾	Combustion with H ₂ at constant volume; pressure about 5 atm.	88.0	-19.74

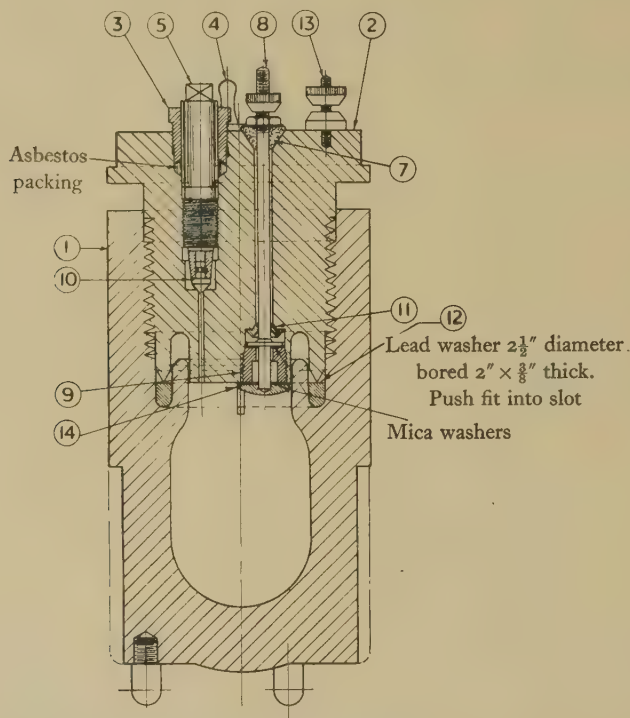
During these investigations, however, it was found that nitrous oxide at a pressure of from 40 to 50 atmospheres can be made to decompose as a mild explosive when initiated by about 0.5 g. of lead azide; on exploring further, it was found that the decomposition can also be produced by fusing a wire in the compressed gas, provided the applied voltage is sufficient to give an arc as the circuit breaks. The latter method has now been applied and will be detailed here.

§ 2. EXPERIMENTAL

Method. Nitrous oxide at a pressure of approximately 42 atmospheres was exploded in a calorimetric closed vessel of stainless steel. The heat produced was measured according to a procedure developed in connexion with the calorimetry of propellants and with which measurements are habitually made to one part in a thousand⁽⁹⁾. Two mercury-in-glass thermometers⁽¹⁰⁾, calibrated to 0.001° C. and certified to 0.002° C.*, were used.

* N.P.L. Ref., Th. 13319.

The closed vessel contained initially nitrous oxide, which was found on analysis to be substantially pure, and finally a mixture which was found to correspond to a decomposition of 90–95 per cent of the original nitrous oxide. The measurement of the heat of formation depended therefore on the precise determination of the quantity and composition of these final products. To determine the mass of nitrous oxide decomposed, three possible methods were available: (i) weighing the nitrous oxide originally taken and determining the amount of nitrous oxide which remained undecomposed; (ii) determining the total free nitrogen produced; and (iii) determining the total free oxygen produced.



Method (i) is limited by the necessarily large mass of the containing vessel, which necessitates the use of a balance capable of taking a load of 10 kg.* It involves also a difficult and somewhat unsatisfactory determination of nitrous oxide in the final gases. As nitrogen is habitually determined by difference, method (ii) also involves this unsatisfactory determination of nitrous oxide in the final gases. Method (iii) is free from these objections, in that the oxygen may be determined directly. The presence of nitrous oxide, however, seriously affects the accuracy of the standard methods of accurate measurement of oxygen-content hitherto employed. This problem has been investigated at some length therefore in this laboratory, and methods have now been evolved for measuring the oxygen-content of the initial and of final gases to within 0.1 per cent.

* The mass of nitrous oxide was approximately 15 gm. See table 6.

The heat of formation has been calculated by each of the three methods. The most accurate figure, that given by method (iii), table 6, has been confirmed, table 7, methods (i) and (ii) within the accuracy obtainable by these latter methods.

Closed vessel. The closed vessel, illustrated in the diagram, was made of Stay-rite steel and had a capacity of 128 cm³. The main seal 12 was made by means of a steel knife-edge and lead washer. The lead was protected from the action of the hot gases by the presence of two narrow annular passages, 0.015 in. and 0.005 in. wide respectively, through which the hot gases had to pass before reaching the lead; by this means the gases were sufficiently cooled, before coming into contact with the lead, for the lead to be unattacked. Inspection of the seal after each experiment showed that no oxidation of lead had occurred.

Water equivalent of calorimetric apparatus. The closed vessel was one of a number used in the calorimetric examination of propellants. When the water equivalent of these was being measured, the possibility of erroneous effects due to reactions between the gases and the steel surfaces was considered, and a diversity of methods were employed for the determination of the water equivalent under varied conditions. These determinations are summarized in table 3, and the effect of the reactions is seen to be inconsiderable.

Table 3. Determination of water equivalent

Method	Water* equivalent (g.)	Number of determinations	Mean difference from mean
Firing 1 g. benzoic and salicylic acids in 100 atm. of oxygen	3769	10	5
Exploding gaseous mixtures containing 22 atm. CO, 11 atm. N ₂ and 67 atm. O ₂ and determining the CO ₂ produced	3771	4	4
Comparing with standard vessel† by firing charges of cordite in an inert atmosphere	3774	4	6
Accepted figure	3771		

* Adjusted to water equivalent = 3 g.

Nitrous oxide. Nitrous oxide of very high purity can now be obtained commercially; the gas used for these measurements was stated by the makers, Messrs Foxeter, London, to be 99.995 per cent pure. A sample for analysis was taken from the closed vessel before firing, and tested for oxygen by a sensitive colorimetric method described elsewhere⁽¹¹⁾. In no case was a figure greater than 0.05 per cent of the nitrous oxide obtained. This procedure served the dual purpose of checking the composition of the nitrous oxide and of showing whether any air had become mixed with it during the process of filling.

Filling of closed vessel. At the beginning of an experiment, the closed vessel, containing 1 cm³ of water† and one atmosphere of air, was weighed. It was then

† The water equivalent of this vessel had been determined both electrically and by the combustion of carbon monoxide⁽⁹⁾.

‡ In order to absorb the small quantities of higher oxides of nitrogen in the products.

evacuated and filled two or three times with nitrous oxide to about 10 atmospheres and the gas released. It was finally filled to about 45 atmospheres.

Method of initiation. Decomposition was initiated by fusing at 50 volts a platinum wire 3 cm. long and 0.012 cm. in diameter. The voltage could be lowered, however, if the production of an arc on fusing was assured by a strongly inductive circuit. The wire was attached by small grooves to two rods of Staybrite steel fixed to the head of the closed vessel. To fire the charge, the circuit was completed and the switch was kept in until, as was shown by an ammeter, the wire fused.

In blank experiments in which the nitrous oxide was replaced by nitrogen or oxygen, the heating effect (4 cal.) was insufficient to be clearly measurable even when it had been magnified by replacing the wire by two similar wires connected in parallel. When a system of smaller thermal capacity was used in the same way, however, rises of 0.004°C. and 0.003°C. were observed, the firing-currents being 8 A. and 6 A. respectively. These rises corresponded to 8 cal. and 6 cal., i.e. to approximately one calorie per ampere. Since this quantity is a small proportion of the total heat, a correction at this rate has been considered adequate.

Measurement of total gas. After each calorimetric measurement, the volume of the final gases was measured by connecting the closed vessel with an evacuated bottle and reading the rise in pressure. The bottle was one of a series of measured volume which are used regularly⁽¹²⁾ for measuring the volumes produced on burning propellants of various compositions. The volumes of the constituent gases were obtained by analysing samples taken separately from the bottle and from the closed vessel*.

Analysis of final products. Gases. Samples from the bottle and from the closed vessel were transferred to a gas-analysis apparatus already described⁽¹³⁾. In the later experiments, (4) to (7), i.e. those from which the accepted result is derived, the oxygen-content was determined in two stages. First about 99.5 per cent of the oxygen was removed by absorption with solid phosphorus confined over mercury⁽¹¹⁾, and next the remainder was determined colorimetrically by means of pyrogallol⁽¹¹⁾. The accuracy of these methods has already been discussed⁽¹¹⁾. The measurements were made in duplicate or triplicate; the error in the figures given in table 6 for the oxygen-content does not exceed 0.1 per cent, and it is considered probable that it may be much smaller than this. In the earlier experiments (1), (2) and (3), the nitrous oxide and oxygen were determined by reduction with excess of carbon monoxide⁽¹²⁾ combined with a density-measurement.

On account of the highly oxidizing nature of the products of explosion, the formation of hydrogen or ammonia from water is precluded. For the same reason nitric oxide is absent. A small proportion of nitrogen dioxide ("peroxide") remains unabsorbed by the water in the closed vessel, and thus occurs in the gases in the bottle. It was determined by bubbling an aliquot part of the gas from the bottle†,

* The proportion of nitrous oxide remaining in the closed vessel was higher than that in the bottle, because the decomposition did not propagate past the narrow annulus at the bottom of the head, and also because on the release of the pressure some nitrous oxide which had been dissolved in the 1 ml. of water in the vessel was released.

† This was done immediately after the gas-measurement.

about 2 litres, through weak hydrogen peroxide acidified with sulphuric acid, determining the nitric acid so formed by the phenoldisulphonic acid method⁽¹⁴⁾. The nitrogen dioxide did not exceed 0.3 per cent on the permanent gas.

In view of the lack of any reliable direct chemical method for the determination of nitrous oxide, a physical method is preferred for the determination of this gas. The large proportional difference between the density of nitrous oxide and that of hydrogen or of oxygen makes the measurement of density a suitable method. The densities were measured by the method of direct weighing⁽¹²⁾ of the gas, with water vapour and nitrogen dioxide removed, in a glass bulb of approximately 600 cm³ capacity, a similar bulb containing dry air being used as a counterpoise. The densities were accurate to ± 0.002 g. per litre, corresponding to ± 0.3 per cent of nitrous oxide in the gas.

Non-gaseous residues in the closed vessel. The closed vessel originally contained 200 ml. of distilled water which absorbed the bulk of the higher oxides of nitrogen. The closed vessel was washed out with distilled water, and an aliquot portion of the washings examined for nitric acid by the Devarda method. In some cases, check tests were made by the phenoldisulphonic acid method. Nitrous acid was shown by these tests never to exceed 1.5 mg.

The closed vessel was then opened and washed out with water, and the nitric acid in the washings was determined. Further portions of the washings were tested for iron and for nickel, in order to check whether the walls of the vessel had been attacked by the nitric acid. The iron did not exceed 1 mg. in any case. Nickel was not detected; 0.03 mg. would have been detected.

Checks on analysis. It was considered desirable at this stage to estimate in the final products the ratio of the total nitrogen to the total oxygen. Since the vessel originally contained pure nitrous oxide, any deviation from 2 of this value is a measure of the limit of reliability of the analytical procedure and the extent to which minor reactions, for instance with the walls of the vessel, may occur.

As is shown in table 4, no consistent deviation has occurred, and the magnitude of the deviations observed is within the estimated limits of measurement.

Table 4. Balance of elements

Number of experiments	Quantities of substances present in closed vessel after firing (cm ³ at n.t.p., molecular volumes being taken as 22.40 litres)							Ratio of nitrogen to oxygen
	N ₂	O ₂	N ₂ O	N ₂ O ₅	NO ₂	Total N (as N ₂)	Total O (as O ₂)	
1	6089	2958	574	39.1	18	6711	3361	1.997
2	6695	3228	533	48.0	19	7285	3634	2.004
3	7099	3417	521	39.8	4	7662	3781	2.026
4	7108	3459	560	39.1	14	7714	3851	2.003
5	7035	3424	590	26.3	12	7657	3797	2.016
6	6812	3341	633	26.3	22	7482	3746	1.997
7	6659	3273	477	28.0	4	7166	3586	1.998
Mean								2.006

Table 5. Effect of formation of nitric acid and nitrogen peroxide on heat and oxygen

Substance	Reaction	Heat produced (cal.) per mg. of substance	Oxygen absorbed per mg. of substance (cm ³ at n.t.p.)
HNO ₃	2N ₂ + 5O ₂ + 2H ₂ O = 4HNO ₃ Aq. + 59.6 Cal.	0.236	0.45
NO ₂	N ₂ + 2O ₂ = 2NO ₂ - 3.4 Cal.	-0.037	0.49

Table 6. Heat of formation of nitrous oxide

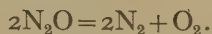
Number of experiment ...	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Estimation of reactant nitrous oxide by measurement of resultant oxygen							
Initial:							
Mass of nitrous oxide (g.)	12.96	14.25	15.11	14.88	15.13	14.82	14.15
% oxygen	—	—	—	<0.01	0.03	0.05	<0.01
Whence, free oxygen initially present (cm ³ at n.t.p.)	—	—	—	<1	2	4	<1
Final:							
Volume of gas measuring bottle (cm ³)	8890	8890	8890	8890	8890	8890	8890
Volume of closed vessel (cm ³)	128	128	128	128	128	128	128
Pressure of gas in bottle and closed vessel (cm. of mercury at 20°C.)	87.26	94.78	100.22	101.36	100.84	98.72	94.62
Temperature (°C.)	19.6	19.4	20.0	21.0	21.6	22.4	20.3
Whence, gas in bottle (cm ³ at n.t.p.)	9488	10310	10883	10970	10894	10635	10262
gas in closed vessel (cm ³ at n.t.p. excluding water vapour)	134	146	154	156	155	151	146
Percentage composition of { gas from bottle	{ O ₂ 30.8 N ₂ O 5.8 N ₂ 63.4	{ O ₂ 30.9 N ₂ O 5.0 N ₂ 64.1	{ O ₂ 31.0 N ₂ O 4.6 N ₂ 64.4	{ O ₂ 31.1 N ₂ O 5.0 N ₂ 63.9	{ O ₂ 31.0 N ₂ O 5.3 N ₂ 63.7	{ O ₂ 31.0 N ₂ O 5.8 N ₂ 63.2	{ O ₂ 31.5 N ₂ O 4.4 N ₂ 64.1
Percentage composition of { gas from closed vessel	{ O ₂ 27.0 N ₂ O 18.0 N ₂ 55.0	{ O ₂ 28.5 N ₂ O 12.5 N ₂ 59.0	{ O ₂ 28.2 N ₂ O 13.0 N ₂ 58.8	{ O ₂ 30.3 N ₂ O 7.0 N ₂ 62.7	{ O ₂ 30.1 N ₂ O 8.2 N ₂ 61.7	{ O ₂ 29.0 N ₂ O 10.5 N ₂ 60.5	{ O ₂ 27.4 N ₂ O 17.0 N ₂ 55.6
Whence free oxygen in bottle and closed vessel (cm ³ at n.t.p.)	2958	3228	3417	3459	3424	3341	3273
Nitric acid in products (g.)	0.220	0.270	0.224	0.220	0.148	0.148	0.157
Nitrogen dioxide in products (g.)	0.037	0.039	0.009	0.028	0.024	0.046	0.009
Whence, Oxygen produced by decomposition of nitrous oxide (cm ³ at n.t.p.)	3075	3368	3522	3572	3503	3431	3433
and, Nitrous oxide decomposed (mol.)	0.2746	0.3007	0.3145	0.3189	0.3129	0.3063	0.299
Measurement of energy							
Temperature rise (°C.)	1.4655	1.595	1.679	1.7076	1.672	1.6375	1.59
Water equivalent (g.)	3767	3771	3771	3771	3767	3771	3771
Whence, total measured heat (cal. ≡ 4.186 joules)	5520	6015	6332	6439	6298	6175	6000
Correction for ignition current (cal.)	12	3	2	9	5	3	3
Correction for nitric acid (cal.)	52	64	53	52	35	35	35
Correction for nitrogen dioxide (cal.)	-1	-1	0	-1	-1	-2	-2
Whence, energy evolved by decomposition of nitrous oxide (cal.)	5457	5949	6277	6379	6259	6139	5960
Hence, Heat of formation of nitrous oxide at constant volume (cal./mol.)	-19.87	-19.78	-19.96	-20.00	-20.00	-20.04	-19.9

Mean (from experiments 1 to 7)
(from experiments 4 to 7)

-19.95 cal./mol.
-20.00 cal./mol.

§ 3. RESULTS

The thermochemistry of the reaction is primarily that of the decomposition of nitrous oxide according to the equation.



It has been found that side reactions are few. These are limited to the formation of higher oxides of nitrogen and their absorption by water; the corrections applied for the energy and volume changes produced by them have been made in accordance with the constants given in table 5.

Table 6 gives the results of seven successive experiments. Of these, numbers (1) to (7) are considered the more reliable because the oxygen figure was obtained by the direct and accurate method developed for the purpose, and because the general technique had become more familiar; the value -20.0_0 cal./mol. at constant volume has therefore been derived from these four experiments*.

Table 7. Heat of formation, reactant mass of nitrous oxide being estimated by alternative (less accurate) methods

Number of experiment	Heat of formation (cal./mol.) at constant volume. Mass N_2O estimated from	
	Weight and residual N_2O	N_2 in products
(1)	-20.2_9	-19.9_1
(2)	-19.8_3	-19.7_4
(3)	-19.6_1	-19.7_0
(4)	-20.3_7	-19.9_7
(5)	-19.7_1	-19.8_4
(6)	-19.8_9	-20.0_8
(7)	-19.8_3	-19.9_9
Mean	-19.9_3	-19.8_9
Mean of (4) to (7)	-19.9_5	-19.9_7

The decomposition of nitrous oxide is accompanied by an increase in volume according to the relation $2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2$. The value of the product pressure \times volume for nitrous oxide at 42 atmospheres has been found to be 0.67 times that for a perfect gas, as described in part III of this paper. For nitrogen and oxygen, the deviation from the value for a perfect gas is not sufficient to affect the final result by one unit in the dropped figure, and is consequently neglected here. The difference between the heats of formation at constant volume and approximately 42 atmospheres and at constant pressure is found from this data to be 0.48 cal./mol.

The heat of formation at constant pressure is thus -19.5_2 cal./mol.

* When the accuracy of these measurements was estimated the determination of oxygen was considered an important limit, and it was not relied upon to closer than 0.1 per cent of the total gas, corresponding to 0.06 cal./mol. in the heat of formation. It is not clear how far the higher accuracy obtained in experiments (4) to (7) is fortuitous, and how far it may be taken as evidence of the higher accuracy of the oxygen determination.

§ 4. DETERMINATION OF HEAT OF FORMATION BY COMBUSTION METHODS AT PRESSURES OF ABOUT 50 ATMOSPHERES

In the course of these investigations, the combustion in nitrous oxide of hydrogen and carbon monoxide were examined at pressures of about 50 atm., and one of us published an early value⁽¹⁵⁾ obtained for the energy of the former reaction. Values for the heat of formation of nitrous oxide deduced from these two reactions were found however to differ by as much as 1 cal./mol., corresponding to 1 per cent on the measured heats.

A further investigation which was thereupon put in hand showed that thermochemical measurements involving the use of hydrogen in steel vessels at pressures of this order, while likely to give consistent results in any single series of measurements, may be misleading on account of absorption^(16, 17) (or in some cases emission) of hydrogen at the walls of the vessel. The behaviour of mild gaseous explosions of this kind is thus similar to what occurs when high explosives are detonated in closed vessels⁽¹⁸⁾; in the case of the former, however, no effects which exceed 1 per cent of the measured value have been detected. In the estimation of the heat of formation of nitrous oxide in this way, 1 per cent on the measured heat of reaction corresponds with $4\frac{1}{2}$ per cent on the heat of formation, and the method becomes an unsatisfactory one.

The mean figure obtained by using carbon monoxide (table 8) was substantially in agreement with the best results obtained by other methods; the variation between individual determinations was, however, considered unsatisfactory.

Table 8. Heat of formation of nitrous oxide by explosion with carbon monoxide in calorimetric closed vessel. Approximate composition: N_2O , 14 atm.; CO , 24 atm.; N_2 , 12 atm.

Measured heat of reaction $N_2O + CO = N_2 + CO_2$	87.2 ₂	86.9 ₂	86.8 ₈	87.2 ₈	87.2 ₁	87.4 ₈	86.7 ₄
Heat of formation of N_2O (cal./mol.) at constant pressure	-19.6 ₀	-19.3 ₀	-19.2 ₄	-19.6 ₈	-19.5 ₉	-19.8 ₈	-19.1 ₂
					Mean	-19.4 ₈	

When nitrous oxide is not present, for instance if oxygen is exploded with excess carbon monoxide⁽⁹⁾, a high order of consistency is obtained, and it would seem that the variability is attributable to some action of the former gas. Nitrous oxide was thus found unsuitable as a substitute for oxygen for thermochemical and calorimetric measurements of the kind for which its use had been proposed.

PART III: THE DEVIATION OF NITROUS OXIDE FROM THE SIMPLE GAS LAWS

BY T. CARLTON-SUTTON AND G. WYN WILLIAMS

The value of the product pressure \times volume has been measured for nitrous oxide at pressures of 1 atmosphere and less by Rayleigh⁽¹⁹⁾ and by Batuecas⁽²⁰⁾. Values of this product at pressures between 40 and 50 atmospheres were required in connexion with the measurement of the heat of formation of this gas. The method devised for this purpose measures the value of this product in terms of that of a standard gas, and has the advantages that the measurements involved are simple and the apparatus required is such as may be found in any laboratory.

To obtain a check on the general accuracy of this method, the values for carbon dioxide were measured in terms of those for nitrogen and compared with the classical values of Amagat⁽²¹⁾, table 9. In view of the agreement thus obtained the method was considered suitable, and the measurements were extended to pressures lower than those employed by Amagat.

Measurements were also made to obtain data for nitrous oxide in terms of those for nitrogen, and from these the deviation of the former gas from the simple gas laws has been deduced.

For any mixture of dry gases, and subject to the restriction that the constituents must act independently in accordance with their partial pressures, the relation between pressure, volume, temperature and mass is given by

$$\Sigma \frac{m}{M} = v \frac{\Sigma \alpha p}{RT},$$

where m is the mass, M the molecular mass and p the partial pressure of each constituent, v is the total volume, T the absolute temperature, R the gas constant, and α the deviation of each gas from Boyle's law expressed as the ratio of the products for the perfect and for the actual gas.

A strong closed vessel of volume v_1 containing a dry gas X at high pressure and a large vessel of volume v_2 containing dry air A at a low pressure p_0 are connected and the pressure changes to p_2 when the contents have mixed isothermally. The total mass remains unchanged and the pressure-volume relations may be obtained by equating the two expressions for this quantity, $\Sigma m/M$, which can be derived from the initial and final conditions.

Initially the mass, $\Sigma m/M$ moles, is

$$\frac{1}{RT} \{x\alpha_1 p_1 v_1 + A\alpha_0 p_0 (g_0 + v_2)\},$$

where the generalized $x\alpha_{lm}$ signifies the deviation of gas X at pressure $(p_l - p_m)$ and g_n signifies the volume of the gauge and connexions at pressure p_n .

Finally, when the gases have mixed, the total pressure p_2 is composed of a partial pressure p_3 of air and a partial pressure $(p_2 - p_3)$ of the gas X , where

$$A\alpha_3 p_3 / A\alpha_0 p_0 = (g_0 + v_2) / (g_2 + v_1 + v_2).$$

m, M, p
 v, T, R
 α

v_1
 p_1, v_2, p_0
 p_2

$x\alpha_{lm}$
 g_n

p_3

The mass $\Sigma m/M$ moles is then

$$\begin{aligned} & \frac{1}{RT} \{ {}_x\alpha_{23} (p_2 - p_3) + {}_A\alpha_3 p_3 \} (v_1 + v_2 + g_2), \\ \text{which} \quad & = \frac{1}{RT} \left\{ {}_x\alpha_{23} \left[(p_2 - p_0) (v_1 + v_2 + g_2) + p_0 v_1 + p_0 (g_2 - g_0) \right. \right. \\ & \quad \left. \left. + p_0 (v_2 + g_0) \left(1 - \frac{{}_A\alpha_0}{{}_A\alpha_3} \right) \right] + {}_A\alpha_0 p_0 (g_0 + v_2) \right\}. \end{aligned}$$

Equating these two expressions for $\Sigma m/M$ we find that

$$p_1 \frac{{}_x\alpha_1}{{}_x\alpha_{23}} = (p_2 - p_0) \frac{v_1 + v_2 + g_2}{v_1} + p_0 + p_0 \frac{g_2 - g_0}{v_1} + p_0 \frac{v_2 + g_0}{v_1} \cdot \frac{{}_A\alpha_3 - {}_A\alpha_0}{{}_A\alpha_3} \dots (1).$$

In a practical case when $p_2 = 1/3$ atm., $p_0 = 1/300$ atm., $v_1 = 128$ cm³, $v_2 = 16$ litres, and $(g_2 - g_0) = 1$ cm³, the second term on the right is less than 0.01 per cent of the first term and the remaining terms are still smaller. For such cases, therefore, all terms but the first may be neglected.

If there is no diffusion of air from the large vessel to the strong closed vessel, the final value of $\Sigma m/M$ may be written

$$\frac{1}{RT} \{ {}_x\alpha_{20} (p_2 - p_0) v_1 + {}_x\alpha_0 p_0 v_1 + {}_x\alpha_{20} (p_2 - p_0) (g_2 + v_2) + {}_A\alpha_0 p_0 (g_2 + v_2) \}$$

and equation (1) becomes

$$p_1 \frac{{}_x\alpha_1}{{}_x\alpha_{20}} = (p_2 - p_0) \frac{v_1 + v_2 + g_2}{v_1} + p_0 \frac{{}_x\alpha_0}{{}_x\alpha_{20}} + p_0 \frac{g_2 - g_0}{v_1} \cdot \frac{{}_A\alpha_0}{{}_A\alpha_{20}}.$$

For this expression, also, all terms but the first may be neglected. In practice, ${}_x\alpha_{20}$ and ${}_x\alpha_{23}$ are to a high order of accuracy equal, and the two expressions consequently become the same. The final values obtained by this method, therefore, are not affected by the amount of diffusion that takes place.

The simple relation obtained by neglecting the small terms in equation (1) involves two pressures p_2 and p_0 which can be measured on an open mercury manometer, and one pressure p_1 which is too great to be measured conveniently in this way. To compare the values of ${}_x\alpha_1/{}_x\alpha_{23}$ with the corresponding values for a standard gas, however, no measurement of this pressure p_1 is required, since if the pressure can be reproduced (without measurement) in two experiments, the relation becomes

$$\alpha' \quad \frac{{}_x\alpha_1}{{}_x\alpha_{23}} / \frac{{}_x\alpha_1'}{{}_x\alpha_{23}'} = \frac{p_2 - p_0}{p_2' - p_0'} \cdot \frac{v_1 + v_2 + g_2}{v_1 + v_2 + g_2'} \dots (2),$$

where the dashes denote that the quantities refer to the standard gas.

The differences between g_2 and g_2' have not exceeded $v_2 \times 10^{-4}$, and the second factor on the right-hand side has consequently been taken as unity.

With considerable accuracy, therefore, ${}_x\alpha_1/{}_x\alpha_{23}$, the ratio of the deviations at pressures p_1 and $(p_2 - p_3)$ respectively, is directly proportional to the measured rise in pressure in the small vessel. When, as in the present cases, the deviation ${}_x\alpha_{23}$ at low pressure is known, the deviation ${}_x\alpha_1$ at any pressure p_1 can be measured in this way.

Table 9

Volume v_1 of small vessel = 128 cm ³ Volume v_2 of bottle = 16.46 litres (except in experiments A and K for which $v_2 = 15.35$ litres)											
Experiments in chronological order...	A	B	C	D	E	F	G	H	K	L	M
Temperature of small vessel... ..	19.6	20.0	19.3	20.1	19.4	19.7	19.0	19.1	18.9	19.1	19.7
Pressure-rise, $p_3 - p_0$ (cm.) in bottle in experiments with											
nitrogen (i) and (v)	12.64	14.62	20.52	17.68	26.29	25.70	23.48	20.59	29.00	5.97	6.99
carbon dioxide (ii) and (iv)	14.26	17.05	26.21	21.43	37.79	36.38	32.03	26.49	41.99	—	7.44
nitrous oxide (iii)	14.44	17.37	26.86	22.00	40.41	38.39	33.11	27.23	45.44	6.37	7.55
Pressure p_1 (atm.) in small vessel indicated approximately on aneroid gauge derived from the measurements with nitrogen	20	25	35	30	45	44	40	35	46	10	11
	19.8	24.6	34.5	29.7	44.0	43.1	39.4	34.5	45.4	10.1	11.8
Values of α_1/α_{23} for nitrogen ^(s) carbon dioxide nitrous oxide	1.006 1.134 1.148	1.007 1.173 1.194	1.008 1.288 1.311	1.008 1.225 1.255	1.010 1.454 1.551	1.010 1.425 1.504	1.009 1.376 1.423	1.008 1.299 1.335	1.010 1.456 1.579	1.003 — 1.073	1.004 1.067 1.084
Value of α_{23} for carbon dioxide ^(s) for nitrous oxide ^(s, 6)	1.001 1.002	1.002 1.002	1.002 1.003	1.002 1.002	1.003 1.005	1.003 1.004	1.003 1.004	1.002 1.003	1.004 1.005	— 1.001	1.001 1.001
α as deduced at above temperatures and pressures for carbon dioxide for nitrous oxide	1.135 1.150	1.175 1.196	1.291 1.315	1.227 1.258	1.458 1.559	1.429 1.510	1.380 1.429	1.301 1.339	1.462 1.587	— 1.074	1.068 1.085
α (Amagat) for carbon dioxide	—	—	—	—	1.450	1.432	1.369	—	1.483	—	—
Ratio p_v actual/ p_v perfect for carbon dioxide for nitrous oxide	0.881 0.870	0.854 0.838	0.775 0.761	0.815 0.795	0.686 0.641	0.790 0.662	0.725 0.700	0.769 0.747	0.684 0.630	— 0.931	0.938 0.921

It is to be noted that equation (2) does not involve p_1 , the initial pressure in the large vessel. In practice, this pressure has been adjusted so as to be the same for the gas under test as for the standard gas; it has not been necessary to measure it directly since the condensation of the standard gas at pressure p_1 is given by the expression $x\alpha_{23}'(p_2' - p_3')v_2/v_1$, and from the known properties of this gas the corresponding value of p_1 can be obtained.

To meet these requirements the following apparatus has been used: A strong closed vessel v_1 of capacity 128 cc., designed for use in the calorimetry of propellants; a large bottle v_2 of capacity 16 litres, which had been carefully calibrated for measurement of the volumes of the gaseous products of explosives; a mercury manometer for the measurement of the pressures, p_0 and p_2 , less than one atmosphere; and an aneroid gauge which, while not measuring the pressure, enabled the vessel v_1 to be filled to the same initial pressure in each of a series of experiments.

A complete series consisted of five experiments in which (i) nitrogen, (ii) carbon dioxide, (iii) nitrous oxide, (iv) carbon dioxide and (v) nitrogen were used successively. Agreement between the first and fifth and the second and fourth experiments has been taken as a sign that the indications of the gauge were satisfactory throughout the series. The results are given in table 9.

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DEMONSTRATION

621.318.5

A RELAY FOR OPERATING TWO CIRCUITS ALTERNATELY WITH DELAYED ACTION
D. S. PERFECT, M.A., D.Phil., National Physical Laboratory

Demonstration given on February 15, 1935

THIS relay was designed to perform in a regular cycle the tilting of a mirror backwards and forwards in order to throw radiation on and off a thermopile. The action is delayed for a definite interval of time after the giving of a warning signal, to enable the observer to take the indication of the thermopile at a particular moment before the change-over occurs. Certain features of the design may have wider interest, since there are several applications in which an alternately acting arrangement is useful with or without delayed action, and this particular instrument has the merit of cheap and simple construction, so that almost anyone could make it for himself.

The general arrangement is shown in figure 1, and certain components in more detail in figures 2, 3 and 4. The details of wiring are omitted as they are fairly obvious and would confuse the diagrams.

M is a synchronous (gramophone) motor run off the 50-cycle, 100-volt mains, and adapted by the addition of the ebonite drum d , and gearing which causes the drum to rotate about a vertical axis at one revolution per second. Let into the surface of the drum is a vertical strip of brass which at every revolution makes electrical contact between two horizontal strips of phosphor bronze sprung into contact with the drum. The dry cell B_1 is thus made to give an impulse every second to the clock C which has a synchronome movement. At the circumference of what would normally be the dial is an annulus r of keramot into which five equally spaced segments of brass are inserted. The internal surface of the short cylindrical tube formed by the annulus is turned in the lathe so that the brass segments are exactly flush with the surface. The segments are in mutual electric connexion. At the end of the hand h is sprung a platinum contact piece which presses against the internal surface of the annulus and follows behind the hand. Thus every 12 seconds for the duration of a second an electric path is opened between the contact piece and one of the brass segments, and a circuit of which these are part is completed.

If the clock had been specially made for the purpose in view it would have been easy to arrange the segments in two sets spaced alternately, so that alternate circuits could be completed which should operate the desired mechanism through simple type of relay. A relay of some kind is necessary because the power required to operate the final mechanism is greater than could be passed directly through the clock without causing destructive sparking. But in point of fact the clock, as also the synchronous motor, was already in use to give simple warning signals every 12 seconds, and thus these two elements were available, in the form

described above, when the details of the method for producing alternate action were in question.

When the circuit through the clock is completed, the dry cell B_2 operates in parallel the buzzer Z and the electromagnet m . The magnet m (see also figure 2)

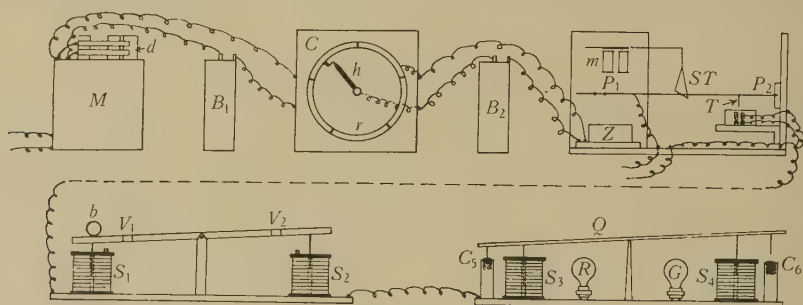


Figure 1.

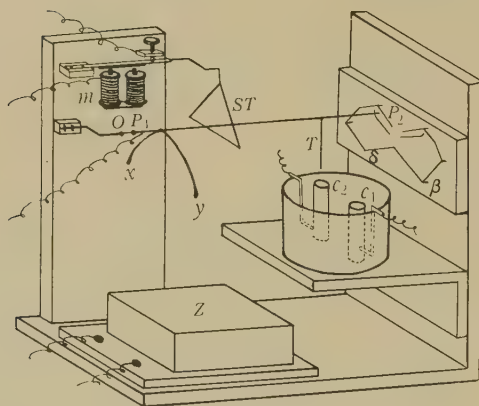


Figure 2.

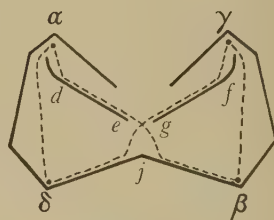


Figure 3.

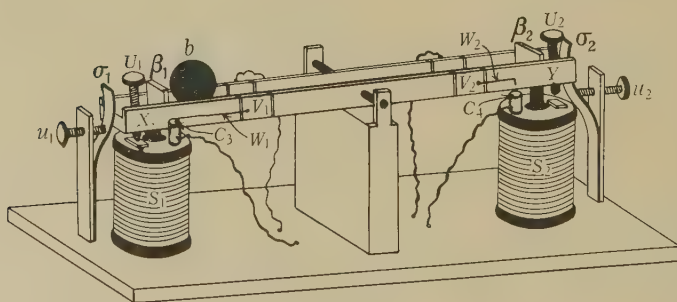


Figure 4.

is part of an electric bell adapted by having a wire stirrup ST soldered to the end of the striking arm in place of the ball. A light rod P_1P_2 , consisting of a piece of steel wire about 20 cm. long and 1 mm. in diameter, is constrained at P_1 by a short length (about 1 mm.) of thread attached to it and to the end of a fixed piece of

ick wire O with sealing-wax. It is constrained by its weight to rest in contact with the horizontal portion of the stirrup ST (the point of contact being about 4 cm. from the end P_1) and about its longitudinal axis by the action of a wire xy fastened to it by sealing wax near the end P_1 . The centre of gravity of the wire is between P_2 and y so that the end x is kept pressed against the vertical face of the wooden upright that holds O and m . Thus the short wire T , which depends from the rod near the end P_2 , is kept approximately vertical. The rod is also constrained near the end P_2 by a system of wires shown in greater detail in figure 3 which is roughly to scale. The system of wires was actually made by inserting ordinary pins into a block of wood and suitably bending them. The range of vertical movement of the stirrup is such that at one extremity the stirrup presses the rod so that the end P_2 is forced into either of the corners α , γ , and at the other extremity leaves it free to rest under gravity in contact with either of the corners β , δ . There are thus four positions of rest which the rod can take up, but the pins are arranged so that these must be reached in a definite cyclic order, namely $\alpha\beta\gamma\delta$, the path of P_2 being shown by the dotted line. For suppose that initially P_2 is at α . When m receives an impulse the stirrup is depressed and the rod falls till it strikes the pin de . It slides down the pin till it reaches the end e when it slips through the gap between e and g . It would now be geometrically possible for it to proceed either to δ or β , but its path is in fact determined mechanically, for in virtue of its horizontal momentum it continues to travel to the right, and by the time it has fallen sufficiently to reach the constraining pins again it is definitely to the right of the dividing edge j and therefore slides down the pin $j\beta$ till it is brought to rest at the corner β . The current supplied to m by the clock lasts for one second, whereas the time taken for the rod to pass from α to β is only a fraction of this. The rod therefore rests at β for the best part of a second. Then the current in m ceases, and the stirrup springs vertically upwards carrying the rod with it. The end P_2 has no choice but to follow a course such as the dotted line till it is brought to rest by the corner γ , where it stays till the next impulse is given by the clock at seconds later. It then proceeds in a similar way from γ to δ and thence back to the starting point α . Two mercury cups c_1 , c_2 , figure 2, are arranged so that when P_2 is at β or δ the wire T is dipping into the corresponding cup. These cups are of glass: each has a T tube of small diameter attached near the bottom and bent upwards. Into the mercury contained in these T tubes iron wires are inserted to make electric connexion. The cups are contained in a cylindrical glass jar which is kept full of distilled water so as completely to submerge them. This arrangement was found to be satisfactory in damping sparks and keeping the mercury clean. It is in this respect far preferable to immersion in oil. The only trouble that arises is that a small quantity of the mercury is atomised by the spark every time the circuit is broken, but this mercury merely collects at the bottom of the jar, and all that is required to maintain the arrangement in working order is the occasional addition of a little mercury to the cups, and of course the periodical addition of distilled water to the jar. The jar rests on a shelf which can be clamped to the wooden upright at the height necessary for correct adjustment of the mercury

cups relative to the wire T . The rod P_1P_2 (by means of a wire attached near the jointed end P_1) and the mercury cups are in circuits (connected through suitable resistance to the 100-volt d.c. mains) which operate one or other of the solenoids S_1, S_2 of figure 4, which shows the arrangement for delayed action. A wooden bar XY is pivoted about its centre. The range of its possible rotation is defined by the adjustable screws U_1, U_2 , the ends of which come up against small brass blocks screwed to the upper faces of the solenoid bobbins. The strip springs σ_1, σ_2 press against the ends of the bar by an amount which can be adjusted by the screws u_1, u_2 , so that the bar just does not slip under the weight of the ball b . Attached to the sides of the bar are two strips of brass the upper edges of which are milled so as to be flat and parallel. They are sawn through in four places so as to give two electrically isolated sections V_1, V_2 . The gaps are filled in with ebonite so that the top edges are mechanically continuous.

Suspended by hooks screwed into the under surface of the bar, two iron rods hang inside the bobbins of the solenoids S_1, S_2 , which are waxed to the base in such positions that the rods hang freely. The solenoids consist of 1-lb. reels of 24 s.w.g. copper wire as commercially supplied. Successive impulses given to the solenoids by the operation of the relay give successive pulls to the iron rods and tilt the bar backwards and forwards. A 1-in. steel Hoffmann ball b rests between the brass rails described above and rolls between two wooden blocks β_1, β_2 which are fixed near the ends in front of the screws U_1, U_2 and act as buffers. The limits of tilt of the bar are adjusted by the screws U_1, U_2 so that the ball, starting from rest at either end, takes the required time, after the impulse is given to the bar, to reach the insulated section at the other end. The sections V_1, V_2 are connected respectively to two solenoids, S_3, S_4 , figure 1, similar to S_1, S_2 and in circuit with the 100-volt mains so that as the ball on its journey from X to Y passes over V_2 it operates the solenoid S_4 . Before reaching V_2 however, the ball must pass the section V_1 , and this would give an impulse to S_3 , but as S_3 was the last to be operated in the previous cycle this additional impulse would cause no reversal. Nevertheless in order to save the total amount of sparking at the rails, and also to eliminate magnetic disturbances which were otherwise set up, and were objectionable for the particular purpose in view, an arrangement was made automatically to cut out this additional impulse. Mercury cups C_3, C_4 , figure 4, are attached to the tops of the bobbins S_1, S_2 respectively, and wires W_1, W_2 are attached to one side of V_1, V_2 respectively, and form parts of the corresponding circuits. The wires are adjusted so that when the end X moves down, W_1 dips into C_3 and W_2 is withdrawn from C_4 , and when the end X moves up, W_1 is withdrawn from C_3 and W_2 is inserted in C_4 . Thus when the end X is down, V_1 is in circuit, but when S_2 tilts the bar this disconnects V_1 before the ball has time to reach it, but puts V_2 in circuit in plenty of time. Sparking at V_1, V_2 is reduced by connecting a condenser across each. Merely for the purpose of demonstrating the working of the system, the solenoids S_3, S_4 were made to tilt backwards and forwards a brass rod Q , figure 1, which made alternate contacts at the mercury cups C_5, C_6 , and lit up alternately a red lamp R and a green lamp G . In the arrangement for which

relay was designed a rod that is operated in a similar way to Q (but without further circuits being involved) works the mechanism referred to in the opening section. In conclusion I should like to thank my colleague, Mr J. Guild, for his interest and assistance in discussing the design at various stages.

NOTE ADDED NOVEMBER 18, 1935

Since the relay was demonstrated in the form described above, the details of construction of the portion which gives delayed action have been somewhat modified.

It was found that the gradual pitting of the surface of the ball which resulted in sparking eventually caused the ball to be retained in its position of rest at the extremity of the bar when the tilt of the bar should have caused it to begin rolling. This was not a very serious trouble since a new ball is easily substituted for the old. But in addition the pitting of the live section of the rail, particularly at the ends of the section where the ebonite is inserted in the gaps, caused the ball to be held up at these points. To remedy this a new bar was made, the rails of which are continuous steel strips. Between the rails at each region corresponding to an insulated section in the previous arrangement is placed a pair of light steel top springs with platinum contacts at the ends. The springs are one above the other, so that in passing over them the ball presses the top spring on to the one below and closes the circuit at the platinum contact. The ball and the rails should last indefinitely, and the platinum contacts can at any time easily be renewed.

REVIEWS

Probability and Random Errors, by W. N. BOND. Pp. viii + 141. (London: Edward Arnold and Co., 1935.) 10s. 6d.

Probability, especially in its application to the theory of errors and the reduction of observations, is as prolific a source of argument and debate as any other branch of philosophy. It would be easy to spend a pleasant evening by the fireside disputing some of the views expressed in this book—or equally pleasant, if one's companion preferred the role of attacker, to pass the hours in defending them.

Point one, to which the debate would frequently return, would be the question whether subsequent knowledge of a more accurate result can be a reason for supposing that one method of treatment of earlier, less accurate, data is better or worse than another treatment. The protagonists would also have the opportunity for a fine clash over the question whether the advice given seventy years ago to astronomers, to help them to decide which observations of parallax (many of which were smaller than their probable errors) ought to be rejected, is of general application. Doubtless, neither side would convert the other but, what is more important, the defender of the book would not at any stage have to repudiate his text.

It can truthfully be said that any readers who contemplate either debating the theory of errors in general or using the methods in reducing observations should certainly be familiar with the contents of this book. Admittedly, it would be well if they were familiar with more, since it is only a ground-work. Within that limitation, however, it is sound and accurate. Among the omitted matters, which might be considered for inclusion in the next edition, are the method of fitting a curve to observations when both coordinates of each point are uncertain, and some sketch of the recent work on goodness of fit.

J. H. A.

A Table of Eisenstein-Reduced Positive Ternary Quadratic Forms of Determinant ≤ 200 , by BURTON W. JONES. 51 pp. (*Bulletin of the National Research Council*, No. 97. Washington, 1935.) \$1.00.

In connexion with the theory of numbers, quadratic forms

$$ax^2 + by^2 + cz^2 + 2ryz + 2syz + 2txy$$

are of interest. Although it is true that by substitutions of the type $X = \alpha_1 x + \beta_1 y + \gamma_1 z$, such a form can in general be transformed into any other quadratic ternary form, yet if the coefficients of the substitution are restricted to be integers, and its determinant $|\alpha_1 \beta_1 \gamma_1|$ to be unity, then the variety of transforms is limited. Of all forms obtainable by such a restricted transformation from a given form, one can be selected as the representative. Eisenstein has shown how to select this reduced form uniquely, and the present table shows the type-forms corresponding to any given form.

Since the determinant of the transformations considered is unity, the determinant

$$\begin{vmatrix} a & t & s \\ t & b & r \\ s & r & c \end{vmatrix}$$

of the form itself is unaltered by the substitution. Thus the basis of the classification is the determinant of the form. For each value of this determinant from 1 to 200, the table shows the values of a , b , c , r , s , and t in the equivalent forms. There may be as many

59 of these reduced forms for a given determinant, and the coefficients for each of the 59 are in such a case given separately. In addition, the actual number of these sub-classes is stated, as well as the number of *automorphs* of each reduced form. (The automorphs of a form are the forms obtained by transformations which turn the form into itself, i.e. the number of automorphs in effect shows the degree of arbitrariness in the actual substitution needed to effect the desired transformation.)

No method is suggested whereby the sub-class can be determined to which a given form belongs, nor is any *process* offered for finding the transformation from a given form to its appropriate reduced form. This is not really necessary, since the purposes for which these forms are used only require that the properties of the reduced form be known. The reduced form is in fact so far representative of all its equivalents, that the properties of both are identical in so far as the applications to number theory are concerned. For this purpose, the present table is admirable. It is more extensive than any precursor, is very clearly arranged, well printed and inexpensive.

J. H. A.

Der Aufbau der Atomkerne (Natürliche und Künstliche Kernumwandlungen), by L. MERTNER and M. DELBRÜCK. Pp. ii+62. (Berlin: Julius Springer, 1935.) RM. 4.50. (Paper cover.)

This is an attractive little book, which can be especially recommended to honours students as an introduction to the study of nuclear physics, and as material for practice in reading German. The first part deals with experimental results, the second with their interpretation in terms of quantum mechanics. The treatment is non-mathematical.

H. R. R.

The Structure of Metallic Coatings, Films and Surfaces. The Sixty-second General Discussion of the Faraday Society, March, 1935. Pp. 248, and 77 plates. (London: Gurney and Jackson, 1935.) 21s. net.

It would be superfluous to emphasize here the value of the discussions held periodically by the Faraday Society on physical and chemical subjects. The high prestige that they have attained in the view of all physicists and chemists as a source of accurate and up-to-date information on many varied topics is a sure guide to their utility. The discussion under review is no exception. Indeed, owing to its practical nature and an almost unique blending of pure and applied science, it is likely to be of even wider interest than many of the previous discussions.

The first half of the discussion, on electron-diffraction, will prove of great value to those interested in this modern development of physics, which, by reason of the results already obtained, may be placed with microscopy as one of the most powerful methods of research available to the metallographer in the study of metal surfaces. Indeed, it is perhaps surprising that a development of such practical importance should have arisen so directly out of the abstruse physical theories of de Broglie. Prof. Finch's complete and beautifully illustrated paper provides an excellent introduction to the method and its applications, while the other papers on this subject also provide material of importance to both physicists and metallographers. Of particular interest is the evidence given by electron-diffraction in favour of Beilby's theory of an amorphous layer on the surface of polished metals.

The second part of the discussion, on metallic coatings, affords a very comprehensive survey of the methods of investigation which may be applied to metal surfaces, in particular to electrodeposited coatings. Optical methods are the subject of two interesting papers by Dr Tronstad and Prof. Ornstein respectively, while others illustrate the metal-

lurgical and X-ray methods of examination. The other papers deal with almost all aspects of electrodeposition in a manner which will doubtless be of interest to both electrochemists and electrodepositors. Finally there are two papers on the formation of coatings by spraying and dipping respectively. It is to be hoped that this discussion will stimulate scientific as against the hitherto rather empirical methods of attacking the problems associated with the production of metallic coatings by electrodeposition and other methods.

No review of this book would be complete without reference to the seventy-seven plates, of which almost half are electron-diffraction photographs. The reproductions are excellent, as indeed is the whole production of the book.

S. F.

The Structure of Crystals. Supplement for 1930-4 to the second edition, by RALPH W. G. WYCKOFF. 240 pp. (American Chemical Society Monograph Series: Reinold Publishing Corporation.) \$ 6.00

Dr Wyckoff's earlier volume contained descriptions of determinations of X-ray structure made previous to and during the year 1930. This supplement continues the account up to the year 1934. Some idea of its scope may be gained by noting that the index of substances contains over 1000 entries, and the bibliography a list of over 2000 papers.

Now that such complex structures are being analysed, the best method of presenting the results in the form of figures is a serious problem. The author gives in most cases a plan of the structure with an indication of the heights of the atoms above the plane of projection, and an accompanying sketch to this same scale in which the atoms are shown as shaded spheres packed together. This scheme is very successful and enables the nature of the structure to be grasped easily.

The Structure of Crystals is one of the essential books of reference for all who work in this field of X-ray analysis, or who need information about crystalline structure. The labour of compiling such a work is great, because authors have many different ways of stating the results of analysis, and each paper must be thoroughly mastered before its contents can be paraphrased into a common conventional form such as is used in the book. We owe a debt of gratitude to Dr Wyckoff for bringing his work up-to-date and so materially assisting the progress of research.

W. L. B.

Infra-red and Raman Spectra, by G. B. B. M. SUTHERLAND, M.A., Ph.D. Pp. xi + 112. (Methuen's Monographs on Physical Subjects. London: Methuen and Co., 1935.) 3s. net.

Though of comparatively recent growth, the two branches of spectroscopy surveyed in this monograph have become so extensive and have assumed such importance in the investigation of the structures of the ground states of polyatomic molecules that each of them needs a considerably larger monograph to itself. Compactness, however, is an avowed and laudable object of this well-known series. In order to condense the essentials of both into 112 small octavo pages, the author treats them as a means of investigation of molecular structure rather than as subjects in themselves. For readers interested in other aspects of these spectra, however, the monograph will be helpful as an introduction. The opening chapter deals with experimental methods, the second chapter with the normal vibrations of molecules of several different types, the next two chapters with non-electronic infra-red absorption bands, i.e. vibration-rotation bands and the far infra-red rotation bands, and the fifth and last chapter with the correlation of these bands and Raman spectra. A bibliography is provided, in addition to references at the end of each chapter. The appendix contains numerical values of internuclear distances, moments of inertia and vibrational frequencies of some molecules in their ground states, as determined from analysis of these spectra.

W. J.

Veröffentlichungen des Wissenschaftlichen Zentral-Laboratoriums der Photographischen Abteilung-Agfa. Band IV. Pp. vi+262. (Leipzig: S. Hirzel, 1935.) RM. 12.50.

The Agfa Company is fortunate in possessing an enthusiastic band of research workers, and the present volume, forming No. 4 of the series of collected papers, contains a number of articles contributed on the occasion of the International Congress for Applied Photography held in Paris this year (1935).

The volume appears to convey a very good idea of the contemporary state of photographic research. We notice papers dealing inter alia with the present theories of the latent image, the measurement of the granularity of developed films, photographic plates for scientific photography, grid lenses, the use of Scheiner disks in Röntgen-ray sensitometry, the resolving-power of photographic objectives, and the cinematographic reproduction of the sensation of space.

It would be quite impossible to deal with more than a small fraction of these topics except in a very long review, but it may be useful to many to know that while perhaps the majority of the articles are addressed to photographic research workers and photographic specialists, there are a number of sections, such as H. K. Weichmann's article on photographic plates for scientific photography which will be of the greatest interest to spectroscopists, microscopists and many others. The spectral sensitivity of various Agfa emulsions is described both verbally and with the aid of step-exposure spectrograms. Both ultra-violet and infra-red plates are described, and the appropriate methods for super-sensitizing the infra-red plates are discussed. The plates described here can be compared with the Ilford products of which short particulars are given in the *Journal of Scientific Instruments* for October, 1935 (p. 333).

Opticians, too, will be interested in Kujawa's article on the resolving-power of photographic objectives in which an interesting attempt is made to develop a method of comparing the relative sharpness of images given by various objectives in a manner really related to the proper conditions of performance. Only too often the results obtained with lens-testing benches can be misinterpreted, and the evolution of a really good test is much to be desired.

The volume is very attractively printed and well illustrated with clear diagrams and photographs.

L. C. M.

Elements of Loud-Speaker Practice, by N. W. McLACHLAN. Pp. viii+160. (Humphrey Milford: The Oxford University Press, 1935.) 5s. net.

If the extent to which an author achieves his purpose is a measure of the success of his book, then Dr McLachlan, who aims at telling "the average person, (1) the purpose of a loud-speaker, (2) how it works, (3) how it is designed, and (4) the effect of the room where it is used upon the sound reproduction", is to be congratulated upon the result of another journalistic venture. The text, which, with the exception of a chapter on recent developments, is derived from a series of articles published in *World Radio* during the latter half of 1933, deals not only with the various forms of loud-speaker but such cognate subjects as baffles and the coupling of the loud-speaker with the power valve. The treatment is authoritative and non-mathematical; the analogies employed are kept within the bounds of the elastic limit; and as the diagrams are as clear as the arguments are lucid the volume, which is well produced and a handbook in the non-teutonic sense, is suitable for relieving the tedium of a train journey. The book should do much to dispel the mist of mixed and doubtful notions with which its subject is apt to be surrounded, and may be recommended both to the "average person" and to those wishing to perceive the loud-speaker wood in true perspective in preparation for a detailed study of any particular tree.

E. J. I.

Noise, by N. W. McLACHLAN. Pp. vi + 148. (Humphrey Milford: The Oxford University Press, 1935.) 6s. net.

As author of this readable little volume Dr McLachlan appears again in his now familiar role of pioneer and provides us with what we believe to be the first book to be published in this country on the subject of noise. The matter is treated from a general rather than a technical standpoint, and the book, dealing as it does with the behaviour of the ear, the measurement of noise and frequency analysis, the noise encountered in various locations and the agencies which produce it, as well as with the physiological and psychological effects of noise and its mitigation, justifies its claim to be a comprehensive survey from every point of view. Although in consequence the book is of the nature of a compilation, the diverse matter it reports—gleaned from some hundred and forty sources cited in an appendix—has been sifted and welded into a well-knit whole. A feature of the text is the use of the expression “reftone level” which conveniently connotes in decibels “the intensity level of the equally loud reference tone of 1000 c./sec. above the datum or threshold of 200 microdynes per cm^2 .” The volume is a companion one to the author’s *Elements of Loud-Speaker Practice*, and, to paraphrase Sir Henry Fowler’s foreword, the book should prove invaluable to those actually interested in the subject as well as to the ordinary man upon whom it is forced.

E. J. I.

Anecdotal History of the Science of Sound, by D. C. MILLER, D.Sc., LL.D. Pp. xii + 114. (London and New York: Macmillan Co., 1935.) 10s. 6d. net.

The author deplores the lack of information on the history of sound given in the text-books, citing two well-known histories of physics in English from which the subject is almost completely omitted. Although we think he would revise his statement if he referred to standard German histories, such as that of Hoppe, it is undoubtedly true that this branch of study was passed over by the majority of physicists until the last few years. No better proof of this statement could be given than the fact that in this country Prof. Miller is more widely known for his ether-drift experiments than for his, probably more extensive, work on the sounds produced by musical instruments.

The book is an attempt to stop this gap in scientific history. It would be unfair to criticize it as a historical treatise, since the author disclaims the intention to write one. The book does in fact give a series of detached notes on the lives and work of experimenters in sound from Pythagoras to W. C. Sabine, i.e. in what one might call, for want of a better classification, pre-War acoustics. It is curious that until the middle of the last century work in sound was almost entirely in the hands of musicians and mathematicians, so that practice and theory pursued separate paths for a longer period than in any other branch of science, except possibly the sister science of hydrodynamics.

The reader of a book like this inevitably finds that his cherished opinions disagree at times with those of the author. For instance, the statement “the flute is the simplest of wind instruments, yet one cannot by theoretical calculation locate any finger-hole on a flute tube which will produce a given tone” is hardly fair to recent applications of Webster’s concept of acoustic impedance, while the summing-up of Rayleigh’s work in the words “Of discoveries sensationally new there is perhaps not one to record, though his experiments have justified many theoretical conclusions and have suggested new points of view” seems rather faint praise of a great scientist. Nevertheless the book is very readable and inspiring, and will undoubtedly form the basis of an historical treatise on sound for whoever is willing to undertake the task of writing one.

E. G. R.

Physics for College Students, by A. A. KNOWLTON, Ph.D., Professor of Physics, Reed College. Second edition. Pp. xxi + 623. (McGraw-Hill Publishing Co., 1935.) 21s. net.

This is an exceptional book in virtue of the general line of treatment adopted by the author, who is an enthusiastic and successful teacher. It is a noteworthy example of an attempt to humanize the subject, by breaking away from the beaten track that has been followed by successions of teachers and pupils whose gaze is turned oft and anon upon calculation requirements, and by seeking rather to reveal the wealth of the subject-matter, attained often by heroic human achievement, and very relevant to the enjoyment of a full life of action and thought.

The course is intended to occupy a year, and to be taken both by those who do and those who do not intend to pursue the subject of physics further during their college career. This is the second edition of the book, and in the intervening seven years the author, while adhering to his main principle of treatment, has made improvements in selection of material and in simplification here and there, as experience has dictated.

One is struck at once by the absence of the usual segregation of phenomena into the domains of mechanics, heat, light, etc., and the idea of a unification soon begins to take shape. Energy occupies a commanding place, and branches, such as radio-electricity, which have recently risen to special importance on account of their attractive applications, or which, like cosmic rays, have made widespread appeal to intellectual curiosity, are given a substantial place.

The mathematical treatment is of the simplest, no mathematics more difficult than simple algebra and trigonometry being drawn upon. Formulae appear in plenty, often without more than a suggestion of the line of proof, but they are clearly explained and justified. Though no previous knowledge of physics is assumed on his part, the student has his attention directed to a vast array of topics which may be of the usual homely kind, such as thermometers, lenses, sound waves, the earth's magnetism, Ohm's law, and so on; or which may belong to categories usually considered abstruse, and outside the range of the elementary student, such as Bernoulli's theorem, the diffraction of light, electric polarization, the Michelson-Morley experiment and the theory of relativity, the equivalence of mass and energy, the quantum of radiation and Planck's constant, and very many more. Teachers would do well to read this book, and to see how it is possible to arouse real intellectual interest and to impart a useful body of knowledge in a field so vast as that of the physics of to-day.

The book is plentifully illustrated with diagrams and photographs, with one coloured plate showing spectra, and the whole is excellently produced. D. O.

Introduction to Physical Science, by CARL W. MILLER. Second Edition. Pp. xiv + 409. (Chapman and Hall.) 15s. net

Prof. Miller emphasizes the close relationships between the classical divisions of physics—heat, light, sound and electricity—and leads the student gradually and easily through no mathematics beyond that common in high school courses to the study and appreciation of such modern subjects as relativity, artificial atomic disintegration, wave mechanics and cosmic physics. The atom and the elementary particles really do get plenty of notice but molecular phenomena are somewhat overlooked; for instance, surface tension is not mentioned. This rather great emphasis on atomic physics would seem to be unfortunate in a book of this standard and generality and with this title.

The aim of the author has been "to lead the student by as natural steps as possible

from the beginnings of scientific thought through to the surprising results of modern research" apparently "in the short space of a single year".

Such ambition merited success and this early publication of a second, somewhat enlarged, edition is an indication that a measure of success has been achieved. J. H. B.

Le Pansoma et la Géométrie de l'Énergie, by Dr A. C. LÉEMAN. Pp. viii + 257. (Genève: Georg et Cie. S.A. Libraires-Éditeurs, Librairie de l'Université, 1935.) Fr. 15.

This book is quite harmless. It contains a large variety of rather feeble speculations which have as their object the unification of recent advances in modern physics, geometry, biology and psychology by the use of the concept of the Pansoma. The author's investigations seem to have no point of contact with the real world and to be exclusively occupied with verbal and numerical jugglery. G. T.

Pareto's General Sociology. A Physiologist's Interpretation, by LAWRENCE J. HENDERSON. 119 pp. (Cambridge Harvard University Press. London: Humphrey Milford, Oxford University Press, 1935.) 5s. 6d. net.

This little book, one half of which is occupied by notes on the text, has been written to provide an introduction to the treatise on General Sociology by Prof. V. Pareto of the University of Lausanne. According to the author, Pareto's researches in sociology have been profoundly influenced by Machiavelli's pioneer study entitled *The Prince*.

This work has a certain interest for students of chemistry and physics inasmuch as the general concept of a physico-chemical system in thermo-dynamical equilibrium is used as an analogy illustrative of Pareto's concept of a general social system; but the analogy is only sketched and, doubtless for very good reasons, receives no systematic development. Pareto's work has already had a certain historical influence as it appears that Signor Mussolini has attributed his abandonment of socialism to the teaching of the author. G. T.

Turbulenz. Physikalische Statistik und Hydrodynamik, by Dr HANS GEBELEIN, V.D.I. 177 pp. (Berlin: Julius Springer, 1935.) RM. 12.50; gebunden RM. 14.

The object of this book is to give a systematic account of the application of statistical methods to the problems of turbulent motion in liquids. The subject is one of immense importance and constitutes the great outstanding problem of physical hydrodynamics as distinct from mathematical hydrodynamics, the main object of which appears to be the construction of elegant and soluble examination questions.

In physical hydrodynamics, in which the object is to investigate the actual properties of real fluids, almost all the difficulties arise from the development of turbulent motion. On the Continent an immense amount of research has been done by Prandtl, von Karman, and by Burgers; while in England we are indebted to G. I. Taylor for a magnificent series of investigations which have recently culminated in the publication of four papers in the issue of the *Proceedings of the Royal Society*, September 2, 1935. Unfortunately the author of this monograph ignores almost entirely the work of G. I. Taylor (whose second initial is given as J.) and the work of Burgers, the only account of which in English is to be found in the first volume of the *Reports on Progress in Physics*, published by the Physical Society. Within these narrow and self-imposed limits, Dr Gebelein gives an admirable account of statistical methods in general and of their application to the extremely

cult and complex problem of turbulent motion. The inclusion in a single monograph of the wide researches of Prandtl and his co-workers is an extremely valuable and important piece of work, and all those who are interested in these hydrodynamical problems will find this book indispensable. G.T.

Low Temperature Physics, by L. C. JACKSON. *High Voltage Physics*, by L. JACOB. Pp. vii + 134. (Methuen's Monographs on Physical Subjects. London: Methuen and Co., 1935.) Each 3s.

This is an age of monographs, for the advances in various branches of physics are so rapid that a comprehensive treatise on physics is often out-of-date in parts before it reaches the public. These small volumes should prove of material assistance to the student preparing for an honours degree and also to the research worker in other branches of physics. In about one hundred pages the field defined by the title of each book is surveyed in a clear and orderly manner.

In the volume on low temperature the subject-matter is restricted to temperatures higher than that of liquid air, and most of it is concerned with the region below 4° K. which is accessible only in specially equipped cryogenic laboratories. We are witnessing in this country at the present day a revived interest in low-temperature research and there is a prospect that this country will regain the supremacy it had a quarter of a century ago, when the Royal Institution was the centre for cryogenic work.

The volume on high-voltage physics is concerned with the effects on matter of voltages of from about 1 kV. to 1000 kV. and more. The opening chapter of the book contains an admirable survey of methods for the production and measurement of high voltages. Most of the results so far obtained on dielectrics are to some extent empirical owing to the complex structure and behaviour of the materials examined. So much investigation work will be necessary before the subject is placed on a theoretical basis. Admirable as these volumes are for the object in view, yet one wishes they could be supplied to the student at a lower price than 3s. per volume. E. G.

Electric Welding Practice, by A. G. ROBIETTE, B.Sc. 324 pp., 87 illustrations, including 3 folding plates. (Charles Griffin and Co., Ltd., 1935.)

With the rapid development in electric-furnace technique that has taken place in recent years, the need has arisen for a new text-book on the subject. The author of the book under review outlines metallurgical practice as carried out in electric melting-furnaces, and discusses the requirements of metallurgical processes in relation to the type of electric furnace which has been found most suitable. The book illustrates the enormous developments that are occurring in the application of electricity to the melting and refining of metals. The subject is one which presents many interesting problems to the physicist in connexion with the design of high-frequency furnaces.

In writing the book, the author has drawn on his experience as metallurgist successively with the Electric Furnace Company, Ltd., and the Birmingham Electric Furnaces, Ltd.

R.G.

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